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54 Insecticidal N'-substituted-N-acyl-N'-alkylcarbonylhydrazines.

57 This invention relates to certain insecticidal N'-substituted-N-acyl-N'-alkylcarbonylhydrazines, compositions containing them and the use of the compounds and compositions as insecticides, especially against insects from the order Lepidoptera and Coleoptera.

INSECTICIDAL N'-SUBSTITUTED-N-ACYL-N'-
ALKYLCARBONYLHYDRAZINES

This invention is concerned with certain N'-substituted-N-acyl-N'-alkylcarbonylhydrazines which are novel compounds useful as insecticides, with compositions containing those compounds and their use as insecticides.

The search for compounds which have a combination of excellent insecticidal activity and low undesirable toxicity continues because of factors such as the desire for compounds of high activity, good selectivity, low undesirable environmental impact, low production cost and effectiveness against insects resistant to many known insecticides.

We have now found certain compounds which are particularly suitable for controlling plant-destructive insects in crops of cultivated plants, ornamentals and forestry.

Certain hydrazine and/or hydrazide derivatives have been disclosed in the following literature which however except in one case as mentioned discloses no biological activity for any of the compounds.

In 25 Aust. J. Chem., 523-529 (1972), several N,N'-dibenzoylhydrazine derivatives are disclosed in which one or both nitrogen atoms are alkylated or phenylated.

In 61 Helv. Chim. Acta, 1477-1510 (1978), several N,N'-dibenzoylhydrazine and hydrazide derivatives are disclosed.

In 44 J.A.C.S., 2556-2567 (1922), isopropyl hydrazine $(\text{CH}_3)_2\text{CH-NH-NH}_2$, symmetrical diisopropyl hydrazine, dibenzoylisopropyl hydrazine and certain derivatives are disclosed.

In 44 J.A.C.S., 1557-1564 (1972), isopropyl, menthyl and bornyl semicarbazides are disclosed.

5 In 48 J.A.C.S., 1030-1035 (1926), symmetrical di-methylphenylmethyl hydrazine and certain related compounds including 1,2-bis-methylphenylmethyl-4-phenyl-semicarbazide are disclosed.

In 27 Bull. Chem. Soc. Japan, 624-627 (1954), certain hydrazine derivatives including alpha,beta-dibenzoylphenyl hydrazine are disclosed.

10 In J. Chem. Soc. (C), 1531-1536 (1966), N,N'-dibenzoylphenyl hydrazine and N-acetyl-N'-benzoyl-p-nitrophenyl hydrazine are disclosed.

In 56B Chem. Berichte, 954-962 (1923), symmetrical di-isopropyl hydrazines, symmetrical diisobutyl and certain derivatives including N,N'-diisobutyldibenzoyl hydrazine are disclosed.

15 In 590 Annalen der Chemie, 1-36 (1954), certain N,N'-dibenzoyl hydrazine derivatives are disclosed including N'-methyl- and N'-(2-phenyl)-isopropyl-N,N'-dibenzoyl hydrazine.

20 In J. Chem. Soc., 4191-4198 (1952), N,N'-di-n-propyl hydrazine and the bis-3,5-dinitrobenzoyl derivatives are disclosed.

In 32 Zhur. Obs. Khim., 2806-2809 (1962), N'-2,4,-methyl-2,4-pentadiene-N,N'-dibenzoyl hydrazine is disclosed.

25 In 17 Acta. Chim. Scand., 95-102 (1963), 2-benzoyl-thiobenzhydrazide ($C_6H_5-CS-NHNH-CO-C_6H_5$) and certain hydrazone and hydrazine derivatives are disclosed including 1,2-dibenzoyl-benzyl hydrazine.

30 In 25 Zhur. Obs. Khim., 1719-1723 (1955), N,N'-bis-cyclohexyl hydrazine and N,N'-dibenzoylcyclohexyl hydrazine are disclosed.

In J. Chem. Soc., 4793-4800 (1964), certain
35 dibenzoyl hydrazine derivatives are disclosed including

tribenzoyl hydrazine and N,N'-dibenzoylcyclohexyl hydrazine.

In 36 J. Prakt. Chem., 197-201 (1967), certain dibenzoyl hydrazine derivatives including N'-ethyl-, N'-n-propyl-, N'-isobutyl-, N'-neopentyl-, N'-n-heptyl-, and N'-cyclohexylmethyl-N,N'-dibenzoyl hydrazines are disclosed.

In 26 J.O.C., 4336-4340 (1961) N'-t-butyl-N,N'-di-(t-butoxycarbonyl) hydrazide is disclosed.

In 41 J.O.C., 3763-3765 (1976), N'-t-butyl-N-(phenylmethoxycarbonyl)-N'-(chlorocarbonyl)hydrazide is disclosed.

In 94 J.A.C.S., 7406-7416 (1972) N'-t-butyl-N,N'-dimethoxycarbonyl hydrazide is disclosed.

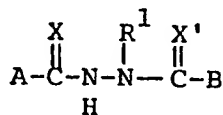
In 43 J.O.C., 808-815 (1978), N'-t-butyl-N-ethoxycarbonyl-N'-phenylaminocarbonyl-hydrazide and N'-t-butyl-N-ethoxycarbonyl-N'-methylaminocarbonyl hydrazide are disclosed.

The N'-substituted-N-acyl-N'-alkylcarbonyl hydrazines of the present invention differ from known compounds primarily by their N- and N'-substituents.

In 39 J. Econ. Ent., 416-417 (1946), certain N-phenyl-N'-acylhydrazines are disclosed and evaluated for their activity against codling moth larvae.

Compounds of the present invention are also distinguished by their excellent insecticidal activity against insects of the orders Lepidoptera and Coleoptera.

The compounds of the invention are those having the formula:



I

wherein

X and X' are the same or different O, S or NR;

R^1 is unsubstituted branched (C_3-C_{10})alkyl or straight chain (C_1-C_4)alkyl substituted with one or two of the same or different (C_3-C_6)cycloalkyl;

A is unsubstituted or substituted naphthyl where the substituents can be from one to three of the same or different halo; cyano; nitro; hydroxy; (C_1-C_4)alkoxy; (C_1-C_4)alkyl; carboxy; (C_1-C_4)alkoxy-carbonyl; (C_1-C_4)-alkanoyloxy; NH_2 ; NH_2 ; or NZZ' ;

unsubstituted or substituted phenyl where the substituents can be from one to five of the same or different halo; nitro; cyano; hydroxy; (C_1-C_6)alkyl; halo-(C_1-C_6)alkyl; cyano-(C_1-C_6)alkyl; (C_1-C_6)alkoxy; halo-(C_1-C_6)alkoxy; (C_1-C_6)alkoxy-(C_1-C_6)alkyl having independently the stated number of carbon atoms in each alkyl group; (C_1-C_6)-alkoxy-(C_1-C_6)alkoxy having independently the stated number of carbon atoms in each alkyl group; $-OCO_2R$ group; (C_2-C_6)alkenyl optionally substituted with halo, cyano, (C_1-C_4)alkyl, (C_1-C_4)alkoxy, halo-(C_1-C_4)-alkoxy or (C_1-C_4)alkylthio; carboxy; $-RCO_2R'$ group; $-COR$ group; halo-(C_1-C_6)-alkyl-carbonyl; cyano(C_1-C_6)alkyl-carbonyl; nitro-(C_1-C_6)alkyl-carbonyl; (C_1-C_6)-alkoxy-carbonyl; halo-(C_1-C_6)-alkoxy-carbonyl; $-OCOR$ group; $-NRR'$; amino substituted with hydroxy, (C_1-C_4)alkoxy or (C_1-C_4)alkylthio groups; phenylamino; diphenylamino; $-CONRR'$ group; $-OCONRR'$ group; $-NRCOR'$ group; $-NRCO_2R'$ group; $-N(COR)COR'$ group; $-OCONRCOR'$ group;

sulphydryl; halothio; (C₁-C₆)alkylthio; halo-(C₁-C₆)alkylthio; -SOR group; -SO₂R group; phenylsulfonyl; -OSO₂R group; halo-(C₁-C₆)alkylsulfonyloxy; -SO₂NRR' group; -NRSOR' group; -NRSO₂R' group; -CSR group; -CS₂R group; -NRCSR' group; -SCOR group; unsubstituted or substituted phenyl having one to three of the same or different halo, cyano, nitro, hydroxy (C₁-C₄)alkyl, (C₁-C₄)alkoxy, carboxy, (C₁-C₄)alkoxy-carbonyl, (C₁-C₄)-alkanoyloxy, NH₂, NHZ, NZZ'; phenoxy where the phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, carboxy, (C₁-C₄)alkoxy-carbonyl, (C₁-C₄)alkanoyloxy, NH₂, NHZ or NZZ'; phenylthio where the phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, carboxy, (C₁-C₄)-alkoxy-carbonyl, (C₁-C₄)alkanoyloxy, NH₂, NHZ or NZZ'; or when two adjacent positions on the phenyl ring are substituted with alkoxy groups, these groups may be joined to form, together with the carbon atoms to which they are both attached, a 5 or 6 membered dioxolano or dioxano heterocyclic ring;

where R, R' and R" are hydrogen or (C₁-C₆)-alkyl, Z and Z' are (C₁-C₄)alkyl and "amino" means NRR';

B is unsubstituted or substituted (C₁-C₁₀)alkyl having one to four of the same or different halo, cyano, nitro, hydroxy, (C₁-C₄)alkoxy, halo-(C₁-C₄)alkoxy, carboxy, (C₁-C₄)-alkoxy-carbonyl, (C₁-C₄)alkanoyloxy, phenyl, NH₂, NHZ or NZZ';

unsubstituted or substituted (C₃-C₈)cycloalkyl or (C₃-C₈)cycloalkyl(C₁-C₄)alkyl, wherein the optional substituents are one to four of the same or different halo, cyano, nitro, hydroxy, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo-(C₁-C₄)alkoxy, carboxy, (C₁-C₄)alkanoyl, (C₁-C₄)alkoxy-carbonyl, (C₁-C₄)alkanoyloxy, phenyl, NH₂, NHZ or NZZ';

unsubstituted or substituted (C₂-C₈)alkenyl or unsubstituted or substituted (C₃-C₈)-alkadienyl having as substituent group(s) a furyl, thienyl or pyridyl group, or one to four of the same or different halo, cyano, nitro, hydroxy, (C₁-C₄)alkyl, (C₃-C₆)-cycloalkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)-alkoxy, halo-(C₁-C₄)alkoxy, carboxy, (C₁-C₄)alkoxy-carbonyl, (C₁-C₄)alkanoyloxy, NH₂, NHZ or NZZ';

unsubstituted or substituted (C₃-C₈)cycloalkenyl or unsubstituted or substituted (C₃-C₈)cycloalkadienyl, having as substituent group(s) one to four of the same or different halo, cyano, nitro, hydroxy, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo-(C₁-C₄)alkoxy, carboxy,

(C₁-C₄)alkoxy-carbonyl, (C₁-C₄)alkanoyloxy, phenyl, NH₂, NHZ or NZZ';

unsubstituted or substituted (C₂-C₈)alkynyl having as optional substituent group(s) one to four of the same or different halo, cyano, nitro, hydroxy, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo-(C₁-C₄)-alkoxy, carboxy, (C₁-C₄)alkoxy-carbonyl, (C₁-C₄)alkanoyloxy, phenyl, NH₂, NHZ or NZZ'; or

phenalkyl having one to four carbon atoms in the alkyl group and wherein the alkyl group is unsubstituted or substituted with one to three of the same or different halo, cyano, hydroxy, (C₁-C₄)alkyl, (C₁-C₄)-alkoxy, (C₁-C₄)alkoxy-carbonyl, NH₂, NHZ or NZZ'; and the phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, cyano-(C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo-(C₁-C₄)alkoxy, carboxy, (C₁-C₄)-alkoxy-carbonyl, (C₁-C₄)alkanoyloxy, (C₂-C₆)alkenyl, halo-(C₂-C₆)alkenyl, (C₂-C₆)alkynyl, NH₂, NHZ or NZZ'; or

phenalkenyl having two to six carbon atoms in the alkenyl group and the alkenyl group is unsubstituted or substituted with one to three of the same or different halo, cyano, hydroxy, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo-(C₁-C₄)alkoxy, (C₁-C₄)-alkoxy-carbonyl, NH₂, NHZ or NZZ'; and the

phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo-(C₁-C₄)alkoxy, carboxy, (C₁-C₄)-alkoxy-carbonyl, (C₁-C₄)alkanoyloxy, NH₂, NHZ or NZZ'; Z and Z' being as above defined;

and agronomically acceptable salts thereof; excluding those compounds wherein X and X' are O, R¹ is t-butyl, A is unsubstituted phenyl and B is unsubstituted methyl or unsubstituted ethyl, which we have found to have little or no insecticidal activity. The invention also provides insecticidal compositions comprising the above compounds together with agronomically acceptable diluent or carrier.

The term "halo" should be understood as including chloro, fluoro, bromo and iodo. The term "alkyl" by itself or as part of another substituent, unless otherwise stated, includes straight or branched chain groups such as methyl, ethyl, n-propyl, isopropyl, n-butyl, t-butyl, isobutyl and neopentyl and, where indicated, higher homologues and isomers such as n-octyl and isooctyl. The term "haloalkyl" by itself or as part of another substituent is an alkyl group of the stated number of carbon atoms having one or more halo atoms bonded thereto such as chloromethyl, 1- or 2-bromoethyl and trifluoromethyl. Analogously, "cyanoalkyl" by itself or as part of another group is an alkyl group of the stated number of carbon atoms having one or more cyano groups bonded thereto; "haloalkoxy" by itself or as part of another group is an alkoxy group of the stated number of carbon atoms having one or more halo atoms bonded thereto, such as difluoromethoxy, trifluoromethoxy, 2-fluoroethoxy and

2,2,2-trifluoroethoxy. "Alkenyl" and "alkynyl" by themselves or as part of another substituent comprise straight and branched chain groups of the stated number of carbon atoms. "Alkadienyl" is a straight or
5 branched chain alkenyl group comprising two carbon-carbon double bonds that can be conjugated such as 1,3-butadienyl, cumulated such as 1,2-propadienyl or isolated such as 1,4-pentadienyl.

Typical compounds within the scope of the present invention which are worthy of mention include, but are not limited to:

10 N'-t-butyl-N-benzoyl-N'-acetylhydrazine
N'-t-butyl-N-benzoyl-N'-propionylhydrazine
N'-t-butyl-N-benzoyl-N'-butyrylhydrazine
15 N'-t-butyl-N-benzoyl-N'-valerylhydrazine
N'-t-butyl-N-benzoyl-N'-hexanoylhydrazine
N'-t-butyl-N-benzoyl-N'-heptanoylhydrazine
N'-t-butyl-N-benzoyl-N'-octanoylhydrazine
N'-t-butyl-N-benzoyl-N'-nonanoylhydrazine
20 N'-t-butyl-N-benzoyl-N'-decanoylhydrazine
N'-t-butyl-N-benzoyl-N'-undecanoylhydrazine
N'-t-butyl-N-benzoyl-N'-cyclopropylcarbonylhydrazine
N'-t-butyl-N-benzoyl-N'-cyclobutylcarbonylhydrazine
N'-t-butyl-N-benzoyl-N'-cyclohexylcarbonylhydrazine
25 N'-t-butyl-N-benzoyl-N'-cycloheptylcarbonylhydrazine
N'-t-butyl-N-benzoyl-N'-cyclooctylcarbonylhydrazine
N'-t-butyl-N-benzoyl-N'-acryloylhydrazine
N'-t-butyl-N-benzoyl-N'-allylcarbonylhydrazine
N'-t-butyl-N-benzoyl-N'-(1-propenylcarbonyl)hydrazine
30 N'-t-butyl-N-benzoyl-N'-crotonoylhydrazine
N'-t-butyl-N-benzoyl-N'-isocrotonoylhydrazine
N'-t-butyl-N-benzoyl-N'-cyclopropenylcarbonylhydrazine
N'-t-butyl-N-benzoyl-N'-cyclobutenylcarbonylhydrazine
N'-t-butyl-N-benzoyl-N'-cyclopentylcarbonylhydrazine
35 N'-t-butyl-N-benzoyl-N'-cyclohexenylcarbonylhydrazine

- N'-t-butyl-N-benzoyl-N'-cycloheptenylcarbonylhydrazine
 N'-t-butyl-N-benzoyl-N'-cyclooctenylcarbonylhydrazine
 N'-t-butyl-N-benzoyl-N'-propioloylhydrazine
 N'-t-butyl-N-benzoyl-N'-(1-butyrylcarbonyl)hydrazine
 5 N'-t-butyl-N-benzoyl-N'-(1-pentynylcarbonyl)hydrazine
 N'-t-butyl-N-benzoyl-N'-(1-hexynylcarbonyl)hydrazine
 N'-t-butyl-N-benzoyl-N'-(1-heptynylcarbonyl)hydrazine
 N'-t-butyl-N-benzoyl-N'-(1-octynylcarbonyl)hydrazine
 N'-t-butyl-N-benzoyl-N'-(2-butyrylcarbonyl)hydrazine
 10 N'-t-butyl-N-benzoyl-N'-(2-pentynylcarbonyl)hydrazine
 N'-t-butyl-N-benzoyl-N'-(3-methyl-1-butyrylcarbonyl)-
 hydrazine
 N'-t-butyl-N-benzoyl-N'-(2-hexynylcarbonyl)hydrazine
 N'-t-butyl-N-benzoyl-N'-(3-hexynylcarbonyl)hydrazine
 15 N'-t-butyl-N-benzoyl-N'-(3,3-dimethyl-1-butyryl-
 carbonyl)hydrazine
 N'-t-butyl-N-benzoyl-N'-(4-octynylcarbonyl)hydrazine
 N'-t-butyl-N-benzoyl-N'-benzylcarbonylhydrazine
 N'-t-butyl-N-benzoyl-N'-phenethylcarbonylhydrazine
 20 N'-t-butyl-N-benzoyl-N'-(3-phenylpropylcarbonyl)-
 hydrazine
 N'-t-butyl-N-benzoyl-N'-(4-phenylbutylcarbonyl)-
 hydrazine
 N'-t-butyl-N-benzoyl-N'-(4-(4-chlorophenyl)butyl-
 25 carbonyl)hydrazine
 N'-t-butyl-N-(4-chlorobenzoyl)-N'-acetylhydrazine
 N'-t-butyl-N-(4-chlorobenzoyl)-N'-propionylhydrazine
 N'-t-butyl-N-(4-chlorobenzoyl)-N'-butyrylhydrazine
 N'-t-butyl-N-(4-chlorobenzoyl)-N'-valerylhydrazine
 30 N'-t-butyl-N-(4-chlorobenzoyl)-N'-hexanoylhydrazine
 N'-t-butyl-N-(4-chlorobenzoyl)-N'-heptanoylhydrazine
 N'-t-butyl-N-(4-chlorobenzoyl)-N'-octanoylhydrazine
 N'-t-butyl-N-(4-chlorobenzoyl)-N'-nonanoylhydrazine
 N'-t-butyl-N-(4-chlorobenzoyl)-N'-decanoylhydrazine
 35 N'-t-butyl-N-(4-chlorobenzoyl)-N'-undecanoylhydrazine

- N'-t-butyl-N-(4-chlorobenzoyl)-N'-cyclopropylcarbonyl-
hydrazine
- N'-t-butyl-N-(4-chlorobenzoyl)-N'-cyclobutylcarbonyl-
hydrazine
- 5 N'-t-butyl-N-(4-chlorobenzoyl)-N'-cyclohexylcarbonyl-
hydrazine
- N'-t-butyl-N-(4-chlorobenzoyl)-N'-cycloheptylcarbonyl-
hydrazine
- 10 N'-t-butyl-N-(4-chlorobenzoyl)-N'-cyclooctylcarbonyl-
hydrazine
- N'-t-butyl-N-(4-chlorobenzoyl)-N'-acryloylhydrazine
- N'-t-butyl-N-(4-chlorobenzoyl)-N'-allylcarbonyl-
hydrazine
- 15 N'-t-butyl-N-(4-chlorobenzoyl)-N'-(1-propenylcarbonyl)-
hydrazine
- N'-t-butyl-N-(4-chlorobenzoyl)-N'-crotonoylhydrazine
- N'-t-butyl-N-(4-chlorobenzoyl)-N'-isocrotonoylhydrazine
- N'-t-butyl-N-(4-chlorobenzoyl)-N'-cyclopropenyl-
carbonylhydrazine
- 20 N'-t-butyl-N-(4-chlorobenzoyl)-N'-cyclobutenylcarbonyl-
hydrazine
- N'-t-butyl-N-(4-chlorobenzoyl)-N'-cyclopentylcarbonyl-
hydrazine
- 25 N'-t-butyl-N-(4-chlorobenzoyl)-N'-cyclohexenylcarbonyl-
hydrazine
- N'-t-butyl-N-(4-chlorobenzoyl)-N'-cycloheptenyl-
carbonylhydrazine
- N'-t-butyl-N-(4-chlorobenzoyl)-N'-cyclooctenylcarbonyl-
hydrazine
- 30 N'-t-butyl-N-(4-chlorobenzoyl)-N'-priprioloylhydrazine
- N'-t-butyl-N-(4-chlorobenzoyl)-N'-(1-butylnylcarbonyl)-
hydrazine
- N'-t-butyl-N-(4-chlorobenzoyl)-N'-(1-pentynylcarbonyl)-
hydrazine

- N'-t-butyl-N-(4-chlorobenzoyl)-N'-(1-hexynylcarbonyl)-
hydrazine
- N'-t-butyl-N-(4-chlorobenzoyl)-N'-(1-heptynylcarbonyl)-
hydrazine
- 5 N'-t-butyl-N-(4-chlorobenzoyl)-N'-(1-octynylcarbonyl)-
hydrazine
- N'-t-butyl-N-(4-chlorobenzoyl)-N'-(2-butyrylcarbonyl)-
hydrazine
- 10 N'-t-butyl-N-(4-chlorobenzoyl)-N'-(2-pentynylcarbonyl)-
hydrazine
- N'-t-butyl-N-(4-chlorobenzoyl)-N'-(3-methyl-1-butyryl-
carbonyl)hydrazine
- N'-t-butyl-N-(4-chlorobenzoyl)-N'-(2-hexynylcarbonyl)-
hydrazine
- 15 N'-t-butyl-N-(4-chlorobenzoyl)-N'-(3-hexynylcarbonyl)-
hydrazine
- N'-t-butyl-N-(4-chlorobenzoyl)-N'-(3,3-dimethyl-1-
butyrylcarbonyl)hydrazine
- N'-t-butyl-N-(4-chlorobenzoyl)-N'-(4-octynylcarbonyl)-
hydrazine
- 20 N'-t-butyl-N-(4-chlorobenzoyl)-N'-benzylcarbonyl-
hydrazine
- N'-t-butyl-N-phenethylcarbonyl-N'-(4-chlorobenzoyl)-
hydrazine
- 25 N'-t-butyl-N-(4-chlorobenzoyl)-N'-(3-phenylpropyl-
carbonyl)hydrazine
- N'-t-butyl-N-(4-chlorobenzoyl)-N'-(4-phenylbutyl-
carbonyl)hydrazine
- N'-t-butyl-N-(4-chlorobenzoyl)-N'-(4-(4-chlorophenyl)-
butylcarbonyl)hydrazine
- 30 N'-t-butyl-N-(3-toluoyl)-N'-acetylhydrazine
- N'-t-butyl-N-(3-toluoyl)-N'-propionylhydrazine
- N'-t-butyl-N-(3-toluoyl)-N'-butyrylhydrazine
- N'-t-butyl-N-(3-toluoyl)-N'-valerylhydrazine
- 35 N'-t-butyl-N-(3-toluoyl)-N'-hexanoylhydrazine

- 5 N'-t-butyl-N-(3-toluoyl)-N'-heptanoylhydrazine
N'-t-butyl-N-(3-toluoyl)-N'-octanoylhydrazine
N'-t-butyl-N-(3-toluoyl)-N'-nonanoylhydrazine
N'-t-butyl-N-(3-toluoyl)-N'-decanoylhydrazine
N'-t-butyl-N-(3-toluoyl)-N'-undecanoylhydrazine
N'-t-butyl-N-(3-toluoyl)-N'-cyclopropylcarbonyl-
hydrazine
N'-t-butyl-N-(3-toluoyl)-N'-cyclobutylcarbonylhydrazine
N'-t-butyl-N-(3-toluoyl)-N'-cyclohexylcarbonylhydrazine
10 N'-t-butyl-N-(3-toluoyl)-N'-cycloheptylcarbonyl-
hydrazine
N'-t-butyl-N-(3-toluoyl)-N'-cyclooctylcarbonylhydrazine
N'-t-butyl-N-(3-toluoyl)-N'-acryloylhydrazine
N'-t-butyl-N-(3-toluoyl)-N'-allylcarbonylhydrazine
15 N'-t-butyl-N-(3-toluoyl)-N'-(1-propenylcarbonyl)-
hydrazine
N'-t-butyl-N-(3-toluoyl)-N'-crotonoylhydrazine
N'-t-butyl-N-(3-toluoyl)-N'-isocrotonoylhydrazine
N'-t-butyl-N-(3-toluoyl)-N'-cyclopropenylcarbonyl-
20 hydrazine
N'-t-butyl-N-(3-toluoyl)-N'-cyclobutenylcarbonyl-
hydrazine
N'-t-butyl-N-(3-toluoyl)-N'-cyclopentylcarbonyl-
hydrazine
25 N'-t-butyl-N-(3-toluoyl)-N'-cyclohexenylcarbonyl-
hydrazine
N'-t-butyl-N-(3-toluoyl)-N'-cycloheptenylcarbonyl-
hydrazine
N'-t-butyl-N-(3-toluoyl)-N'-cyclooctenylcarbonyl-
30 hydrazine
N'-t-butyl-N-(3-toluoyl)-N'-propioloylhydrazine
N'-t-butyl-N-(3-toluoyl)-N'-(1-butylnylcarbonyl)-
hydrazine
N'-t-butyl-N-(3-toluoyl)-N'-(1-pentynylcarbonyl)-
35 hydrazine

- N'-t-butyl-N-(3-toluoyl)-N'-(1-hexynylcarbonyl)-
hydrazine
- N'-t-butyl-N-(3-toluoyl)-N'-(1-heptynylcarbonyl)-
hydrazine
- 5 N'-t-butyl-N-(3-toluoyl)-N'-(1-octynylcarbonyl)-
hydrazine
- N'-t-butyl-N-(3-toluoyl)-N'-(2-butyrylcarbonyl)-
hydrazine
- N'-t-butyl-N-(3-toluoyl)-N'-(2-pentynylcarbonyl)-
10 hydrazine
- N'-t-butyl-N-(3-toluoyl)-N'-(3-methyl-1-butyryl-
carbonyl)hydrazine
- N'-t-butyl-N-(3-toluoyl)-N'-(2-hexynylcarbonyl)-
hydrazine
- 15 N'-t-butyl-N-(3-toluoyl)-N'-(3-hexynylcarbonyl)-
hydrazine
- N'-t-butyl-N-(3-toluoyl)-N'-(3,3-dimethyl-1-butyryl-
carbonyl)hydrazine
- N'-t-butyl-N-(3-toluoyl)-N'-(4-octynylcarbonyl)-
20 hydrazine
- N'-t-butyl-N-(3-toluoyl)-N'-benzoylcarbonylhydrazine
- N'-t-butyl-N-(3-toluoyl)-N'-phenethylcarbonylhydrazine
- N'-t-butyl-N-(3-toluoyl)-N'-(3-phenylpropylcarbonyl)-
hydrazine
- 25 N'-t-butyl-N-(3-toluoyl)-N'-(4-phenylbutylcarbonyl)-
hydrazine
- N'-t-butyl-N-(3-toluoyl)-N'-(4-(4-chlorophenyl)butyl-
carbonyl)hydrazine
- N'-t-butyl-N-(2-methoxybenzoyl)-N'-acetylhydrazine
- 30 N'-t-butyl-N-(2-methoxybenzoyl)-N'-propionylhydrazine
- N'-t-butyl-N-(2-methoxybenzoyl)-N'-butyrylhydrazine
- N'-t-butyl-N-(2-methoxybenzoyl)-N'-valerylhydrazine
- N'-t-butyl-N-(2-methoxybenzoyl)-N'-hexanoylhydrazine
- N'-t-butyl-N-(2-methoxybenzoyl)-N'-heptanoylhydrazine
- 35 N'-t-butyl-N-(2-methoxybenzoyl)-N'-octanoylhydrazine

- 5 N'-t-butyl-N-(2-methoxybenzoyl)-N'-nonanoylhydrazine
N'-t-butyl-N-(2-methoxybenzoyl)-N'-decanoylhydrazine
N'-t-butyl-N-(2-methoxybenzoyl)-N'-undecanoylhydrazine
N'-t-butyl-N-(2-methoxybenzoyl)-N'-cyclopropylcarbonyl-
hydrazine
N'-t-butyl-N-(2-methoxybenzoyl)-N'-cyclobutylcarbonyl-
hydrazine
N'-t-butyl-N-(2-methoxybenzoyl)-N'-cyclohexylcarbonyl-
hydrazine
10 N'-t-butyl-N-(2-methoxybenzoyl)-N'-cycloheptylcarbonyl-
hydrazine
N'-t-butyl-N-(2-methoxybenzoyl)-N'-cyclooctylcarbonyl-
hydrazine
N'-t-butyl-N-(2-methoxybenzoyl)-N'-acryloylhydrazine
15 N'-t-butyl-N-(2-methoxybenzoyl)-N'-allylcarbonyl-
hydrazine
N'-t-butyl-N-(2-methoxybenzoyl)-N'-(1-propenyl-
carbonyl)hydrazine
N'-t-butyl-N-(2-methoxybenzoyl)-N'-crotonoylhydrazine
20 N'-t-butyl-N-(2-methoxybenzoyl)-N'-isocrotonoyl-
hydrazine
N'-t-butyl-N-(2-methoxybenzoyl)-N'-cyclopropenyl-
carbonylhydrazine
N'-t-butyl-N-(2-methoxybenzoyl)-N'-cyclobutenyl-
carbonylhydrazine
25 N'-t-butyl-N-(2-methoxybenzoyl)-N'-cyclopentylcarbonyl-
hydrazine
N'-t-butyl-N-(2-methoxybenzoyl)-N'-cyclohexenyl-
carbonylhydrazine
30 N'-t-butyl-N-(2-methoxybenzoyl)-N'-cycloheptenyl-
carbonylhydrazine
N'-t-butyl-N-(2-methoxybenzoyl)-N'-cyclooctenyl-
carbonylhydrazine
N'-t-butyl-N-(2-methoxybenzoyl)-N'-propioloylhydrazine

- N'-t-butyl-N-(2-methoxybenzoyl)-N'-(1-butynylcarbonyl)-hydrazine
- N'-t-butyl-N-(2-methoxybenzoyl)-N'-(1-pentynylcarbonyl)hydrazine
- 5 N'-t-butyl-N-(2-methoxybenzoyl)-N'-(1-hexynylcarbonyl)-hydrazine
- N'-t-butyl-N-(2-methoxybenzoyl)-N'-(1-heptynylcarbonyl)hydrazine
- 10 N'-t-butyl-N-(2-methoxybenzoyl)-N'-(1-octynylcarbonyl)-hydrazine
- N'-t-butyl-N-(2-methoxybenzoyl)-N'-(2-butynylcarbonyl)-hydrazine
- N'-t-butyl-N-(2-methoxybenzoyl)-N'-(2-pentynylcarbonyl)hydrazine
- 15 N'-t-butyl-N-(2-methoxybenzoyl)-N'-(3-methyl-1-butynylcarbonyl)hydrazine
- N'-t-butyl-N-(2-methoxybenzoyl)-N'-(2-hexynylcarbonyl)-hydrazine
- N'-t-butyl-N-(2-methoxybenzoyl)-N'-(3-hexynylcarbonyl)-hydrazine
- 20 N'-t-butyl-N-(2-methoxybenzoyl)-N'-(3,3-dimethyl-1-butynylcarbonyl)hydrazine
- N'-t-butyl-N-(2-methoxybenzoyl)-N'-(4-octynylcarbonyl)-hydrazine
- 25 N'-t-butyl-N-(2-methoxybenzoyl)-N'-benzylcarbonylhydrazine
- N'-t-butyl-N-(2-methoxybenzoyl)-N'-phenethylcarbonylhydrazine
- N'-t-butyl-N-(2-methoxybenzoyl)-N'-(3-phenylpropylcarbonyl)hydrazine
- 30 N'-t-butyl-N-(2-methoxybenzoyl)-N'-(4-phenylbutylcarbonyl)hydrazine
- N'-t-butyl-N-(2-methoxybenzoyl)-N'-(4-(4-chlorophenyl)butylcarbonyl)hydrazine
- 35 N'-t-butyl-N-(3-fluorobenzoyl)-N'-acetylhydrazine

- N'-t-butyl-N-(3-fluorobenzoyl)-N'-propionylhydrazine
N'-t-butyl-N-(3-fluorobenzoyl)-N'-butyrylhydrazine
N'-t-butyl-N-(3-fluorobenzoyl)-N'-valerylhydrazine
N'-t-butyl-N-(3-fluorobenzoyl)-N'-hexanoylhydrazine
N'-t-butyl-N-(3-fluorobenzoyl)-N'-heptanoylhydrazine
5 N'-t-butyl-N-(3-fluorobenzoyl)-N'-octanoylhydrazine
N'-t-butyl-N-(3-fluorobenzoyl)-N'-nonanoylhydrazine
N'-t-butyl-N-(3-fluorobenzoyl)-N'-decanoyl(3-fluoro-
benzoyl)hydrazine
N'-t-butyl-N-(3-fluorobenzoyl)-N'-undecanoylhydrazine
10 N'-t-butyl-N-(3-fluorobenzoyl)-N'-cyclopropylcarbonyl-
hydrazine
N'-t-butyl-N-(3-fluorobenzoyl)-N'-cyclobutylcarbonyl-
hydrazine
N'-t-butyl-N-(3-fluorobenzoyl)-N'-cyclohexylcarbonyl-
15 hydrazine
N'-t-butyl-N-(3-fluorobenzoyl)-N'-cycloheptylcarbonyl-
hydrazine
N'-t-butyl-N-(3-fluorobenzoyl)-N'-cyclooctylcarbonyl-
hydrazine
20 N'-t-butyl-N-(3-fluorobenzoyl)-N'-acryloylhydrazine
N'-t-butyl-N-(3-fluorobenzoyl)-N'-allylcarbonyl-
hydrazine
N'-t-butyl-N-(3-fluorobenzoyl)-N'-(1-propenylcarbonyl)-
hydrazine
25 N'-t-butyl-N-(3-fluorobenzoyl)-N'-crotonoylhydrazine
N'-t-butyl-N-(3-fluorobenzoyl)-N'-isocrotonoylhydrazine
N'-t-butyl-N-(3-fluorobenzoyl)-N'-cyclopropenyl-
carbonylhydrazine
N'-t-butyl-N-(3-fluorobenzoyl)-N'-cyclobutenylcarbonyl-
30 hydrazine
N'-t-butyl-N-(3-fluorobenzoyl)-N'-cyclopentylcarbonyl-
hydrazine
N'-t-butyl-N-(3-fluorobenzoyl)-N'-cyclohexenylcarbonyl-
hydrazine

- N'-t-butyl-N-(3-fluorobenzoyl)-N'-cycloheptenyl-
carbonylhydrazine
- N'-t-butyl-N-(3-fluorobenzoyl)-N'-cyclooctenylcarbonyl-
hydrazine
- 5 N'-t-butyl-N-(3-fluorobenzoyl)-N'-propioloylhydrazine
- N'-t-butyl-N-(3-fluorobenzoyl)-N'-(1-butylnylcarbonyl)-
hydrazine
- N'-t-butyl-N-(3-fluorobenzoyl)-N'-(1-pentylnylcarbonyl)-
hydrazine
- 10 N'-t-butyl-N-(3-fluorobenzoyl)-N'-(1-hexylnylcarbonyl)-
hydrazine
- N'-t-butyl-N-(3-fluorobenzoyl)-N'-(1-heptylnylcarbonyl)-
hydrazine
- N'-t-butyl-N-(3-fluorobenzoyl)-N'-(1-octylnylcarbonyl)-
- hydrazine
- 15 N'-t-butyl-N-(3-fluorobenzoyl)-N'-(2-butylnylcarbonyl)-
hydrazine
- N'-t-butyl-N-(3-fluorobenzoyl)-N'-(2-pentylnylcarbonyl)-
hydrazine
- 20 N'-t-butyl-N-(3-fluorobenzoyl)-N'-(3-methyl-1-butylnyl-
carbonyl)hydrazine
- N'-t-butyl-N-(3-fluorobenzoyl)-N'-(2-hexylnylcarbonyl)-
hydrazine
- N'-t-butyl-N-(3-fluorobenzoyl)-N'-(3-hexylnylcarbonyl)-
hydrazine
- 25 N'-t-butyl-N-(3-fluorobenzoyl)-N'-(3,3-dimethyl-1-
butylnylcarbonyl)hydrazine
- N'-t-butyl-N-(3-fluorobenzoyl)-N'-(4-octylnylcarbonyl)-
hydrazine
- 30 N'-t-butyl-N-(3-fluorobenzoyl)-N'-benzylcarbonyl-
hydrazine
- N'-t-butyl-N-(3-fluorobenzoyl)-N'-phenethylcarbonyl-
hydrazine
- N'-t-butyl-N-(3-fluorobenzoyl)-N'-(3-phenylpropyl-
carbonyl)hydrazine
- 35

Because of their good insecticidal activity,
preferred compounds include those where, independently

X and X' are O or S; and/or

R¹ is unsubstituted (C₃-C₈) branched alkyl or a
(C₁-C₄) straight chain alkyl substituted
with one or two of the same or different
(C₃-C₄) cycloalkyl; and/or

A is unsubstituted naphthyl; or

unsubstituted or substituted phenyl where
the substituents can be from one to three
of the same or different halo; nitro;
cyano; (C₁-C₄) alkyl; halo-(C₁-C₄) alkyl;
(C₁-C₄) cyanoalkyl; (C₁-C₄) alkoxy; (C₁-C₄)-
alkoxy-(C₁-C₄) alkyl; -COD; carboxy;
(C₁-C₄) alkoxy-carbonyl; (C₁-C₄) alkanoyloxy;
NH₂, NHZ or NZZ'; (C₁-C₄) alkylthio; -CSD;
-CS₂D; -SCOD; unsubstituted or substituted
phenyl having one to two of the same or
different halo, nitro, (C₁-C₄) alkyl,
(C₁-C₄) alkoxy, carboxy, (C₁-C₄)-
alkoxy-carbonyl, (C₁-C₄)- alkanoyloxy, NH₂,
NHZ or NZZ'; phenoxy where the phenyl ring
is unsubstituted or substituted with one or
two of the same or different halo, nitro,
(C₁-C₄) alkyl, (C₁-C₄) alkoxy, carboxy,
(C₁-C₄)- alkoxy-carbonyl, (C₁-C₄)-
alkanoyloxy, NH₂, NHZ or NZZ'; or when two
adjacent positions on the phenyl ring are
substituted with alkoxy groups, these
groups may be joined to form, together with
the carbon atoms to which they are both
attached, a 5- or 6-membered dioxolano or
dioxano heterocyclic ring; and/or

- N'-t-butyl-N-(3-fluorobenzoyl)-N'-(4-phenylbutyl-carbonyl)hydrazine
- N'-t-butyl-N-(3-fluorobenzoyl)-N'-(4-(4-chlorophenyl)-butylcarbonyl)hydrazine
- 5 N'-t-butyl-N-benzoyl-N'-(1-carboethoxy-2-hydroxy-propionyl)hydrazine
- N'-t-butyl-N-(2,3-dimethylbenzoyl)-N'-(3-cyclohexenyl-carbonyl)hydrazine
- 10 N'-t-butyl-N-(2,3-dimethylbenzoyl)-N'-(2-(4-chloro-phenyl)-3-methylbutanoyl)hydrazine
- N'-t-butyl-N-benzoyl-N'-(2-methylcyclohexadi-2,5-enyl-carbonyl)hydrazine
- N'-t-butyl-N-benzoyl-N'-phenylpropynoylhydrazine
- N'-t-butyl-N-benzoyl-N'-(2-methylbutanoyl)hydrazine
- 15 N'-t-butyl-N-benzoyl-N'-(2-phenyl-3-methylpentanoyl)-hydrazine
- N'-t-butyl-N-benzoyl-N'-(3-acetyl-2,2-dimethylcyclo-butyl)-methylcarbonyl)hydrazine
- N'-t-butyl-N-benzoyl-N'-(2-pentenoyl)hydrazine
- 20 N'-t-butyl-N-benzoyl-N'-(4-pentenoyl)hydrazine
- N'-t-butyl-N-benzoyl-N'-(4-carbomethoxybutanoyl)-hydrazine
- N'-t-butyl-N-benzoyl-N'-methoxyacetylhydrazine
- N'-t-butyl-N-(2,3-dimethylbenzoyl)-N'-methacryloyl-hydrazine
- 25 N'-t-butyl-N-(4-ethylbenzoyl)-N'-methacryloylhydrazine
- N'-t-butyl-N-(2,3-dimethylbenzoyl)-N'-(2-methyl-propionyl)hydrazine
- N'-t-butyl-N-(2,3-dimethylbenzoyl)-N'-(2,2-dimethyl-propionyl)hydrazine
- 30 N'-t-butyl-N-(2,3-dimethylbenzoyl)-N'-(2-ethyl-acryloyl)hydrazine
- N'-t-butyl-N-(2,3-dimethylbenzoyl)-N'-(2-methyl-2-pentenoyl)hydrazine

B is unsubstituted or substituted (C₁-C₈)alkyl having one to three of the same or different halo, cyano, (C₁-C₄)alkoxy, phenyl, (C₁-C₄)alkoxy-carbonyl or halo-(C₁-C₄)alkoxy;

unsubstituted or substituted (C₃-C₆)cycloalkyl or (C₃-C₆)cycloalkyl(C₁-C₄)alkyl, wherein the optional substituents are one or two of the same or different halo, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy (C₁-C₄)alkanoyl or halo-(C₁-C₄)alkoxy;

unsubstituted or substituted (C₂-C₆)alkenyl having a furyl or one to three of the same or different (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy or halo-(C₁-C₄)alkoxy;

unsubstituted or substituted (C₃-C₆)cycloalkenyl having one or two of the same or different halo, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy or halo-(C₁-C₄)alkoxy;

unsubstituted or phenyl-substituted alkynyl; phenalkyl having one or two carbon atoms in the alkyl group and the alkyl group is unsubstituted or substituted with one or two of the same or different halo, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy or halo-(C₁-C₄)alkoxy and the phenyl ring is unsubstituted or substituted with one or two of the same or different halo, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy or halo-(C₁-C₄)alkoxy;

alkoxy or halo-(C₁-C₄)alkoxy; or

phenalkenyl having two or three carbon atoms in the alkenyl group and the alkenyl group is unsubstituted or substituted with halo, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy or halo-(C₁-C₄)alkoxy and the phenyl ring is unsubstituted or substituted with one or two of the same or different halo, cyano, (C₁-C₄)alkyl, halo-(C₁-C₄)-alkyl, (C₁-C₄)alkoxy or halo-(C₁-C₄)alkoxy;

where D is hydrogen or (C₁-C₄)alkyl and Z and Z' are (C₁-C₄)alkyl; and agronomically acceptable salts thereof.

More preferred insecticidal compounds of the invention, include those where, independently,

X and X' are O or S; and/or

R¹ is branched (C₃-C₈)alkyl; and/or

A is unsubstituted naphthyl;

unsubstituted or substituted phenyl having one to three of the same or different halo; nitro; cyano; (C₁-C₄)alkyl; halo-(C₁-C₄)-alkyl; cyano-(C₁-C₄)alkyl; (C₁-C₄)alkoxy; -COD; (C₁-C₄)alkoxy-carbonyl; (C₁-C₄)-alkanoyloxy; or unsubstituted or

substituted phenyl having one or two of the same or different halo, nitro, (C₁-C₄)-alkyl, (C₁-C₄)alkoxy, carboxy, (C₁-C₄)-alkoxy-carbonyl, (C₁-C₄)alkanoyloxy, NH₂, NHZ or NZZ'; where D is hydrogen or (C₁-C₄)alkyl; and/or

5 B is unsubstituted or substituted (C₁-C₆)alkyl
having one to three of the same or
different halo, cyano, (C₁-C₄)alkoxy,
phenyl, (C₁-C₄)alkoxy-carbonyl or halo-
(C₁-C₄)alkoxy;

10 unsubstituted or substituted (C₃-C₆)-
cycloalkyl or (C₃-C₆)cycloalkyl(C₁-C₄)-
alkyl, wherein the optional substituent is
halo (C₁-C₄)alkyl, (C₁-C₄)alkanoyl,
(C₁-C₄)alkoxy or halo-(C₁-C₄)alkoxy;

unsubstituted or substituted (C₂-C₆)alkenyl
having one or two of the same or different
(C₁-C₄)alkyl, (C₁-C₄)alkoxy or halo-
(C₁-C₄)alkoxy;

15 unsubstituted or substituted (C₄-C₆)cyclo-
alkenyl where the substituent is halo,
(C₁-C₄)alkyl, (C₁-C₄)alkoxy or halo-
(C₁-C₄)alkoxy; or

20 unsubstituted or phenyl-substituted
alkynyl;

and agronomically acceptable salts thereof.

25 Because of their excellent insecticidal
activity, particularly preferred compounds of the
present invention for use in the insecticidal
compositions and formulations of the present invention
include those where, independently,

X and X' are O; and/or

R¹ is branched (C₄-C₇)alkyl; and/or

30 A is unsubstituted, mono-substituted 2,3-
disubstituted or 2,4-disubstituted phenyl

where the substituents can be the same or different halo, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, or halo-(C₁-C₄)alkyl; and/or

B is unsubstituted or substituted (C₁-C₆)alkyl having one to three of the same or different halo, phenyl or cyano;

unsubstituted (C₄-C₆)cycloalkyl;

unsubstituted or substituted (C₂-C₅)alkenyl having as the optional substituent(s) one or two of the same or different (C₁-C₄)alkyl;

unsubstituted (C₄-C₆)cycloalkenyl; or

phenalkyl having one or two carbon atoms in the alkyl group and the phenyl ring is unsubstituted or substituted with one or two of the same or different halo, (C₁-C₄)alkyl, or (C₁-C₄)alkoxy; and

agronomically acceptable salts thereof.

Because of their outstanding insecticidal activity, most preferred compounds of the present invention for use in the insecticidal compositions and formulations of the present invention include those where, independently,

X and X' are O; and/or

R¹ is t-butyl, neopentyl (2,2-dimethylpropyl) or 1,2,2-trimethylpropyl; and/or

A is unsubstituted or mono-substituted phenyl where the substituent can be chloro, fluoro, bromo, iodo, methyl, ethyl, methoxy or trifluoromethyl; and/or

B is unsubstituted or substituted (C_1-C_4)alkyl having one to three of the same or different phenyl, chloro, fluoro or bromo;

unsubstituted (C_4-C_6)cycloalkyl;

5 unsubstituted (C_4-C_6)cycloalkenyl; or

phenalkyl having one to two carbon atoms in the alkyl group and the phenyl ring is unsubstituted or substituted with one or two of the same or different chloro,
10 fluoro, bromo, iodo, methyl, ethyl, methoxy or trifluoromethyl; and

agronomically acceptable salts thereof.

Those N'-substituted-N-acyl-N'-alkylcarbonyl hydrazines of Formula I which possess acidic or basic
15 functional groups may be further reacted to form novel salts with appropriate bases or acids. These salts also exhibit insecticidal activity. Typical salts are the agronomically acceptable metal salts, ammonium salts and acid addition salts. Among the metal salts
20 are those in which the metal cation is an alkali metal cation such as sodium, potassium, lithium or the like; alkaline earth metal cation such as calcium, magnesium, barium, strontium or the like; or heavy metal cation such as zinc, manganese, cupric, cuprous, ferric,
25 ferrous, titanium, aluminum or the like. The ammonium salts include those in which the ammonium cation has the formula $NR^5R^6R^7R^8$ wherein each of R^5 , R^6 , R^7 and R^8 are independently hydrogen, hydroxy, (C_1-C_4)alkoxy, (C_1-C_{20})alkyl, (C_3-C_8)alkenyl, (C_3-C_8)alkynyl, (C_2-C_8)hydroxyalkyl, (C_2-C_8)alkoxyalkyl, (C_2-C_6)aminoalkyl,
30 (C_2-C_6)haloalkyl, NH_2 , (C_1-C_4)alkyl- or di(C_1-C_4)alkyl-

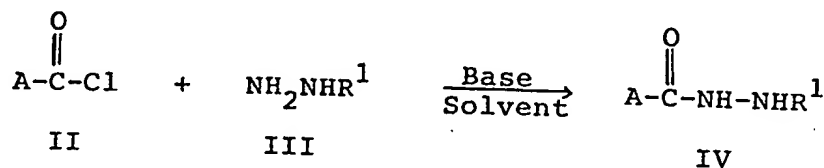
amino, substituted or unsubstituted phenyl, substituted or unsubstituted phenylalkyl, having up to four carbon atoms in the alkyl moiety, or any two of R^5 , R^6 , R^7 or R^8 can be taken together to form with the nitrogen atom a 5- or 6- membered heterocyclic ring, optionally having up to one additional hetero atom (e.g., oxygen, nitrogen, or sulfur) in the ring, and preferably saturated, such as piperidino, morpholino, pyrrolidino or piperazino, or any three of R^5 , R^6 , R^7 or R^8 can be taken together to form with the nitrogen atom a 5- or 6-membered aromatic heterocyclic ring, such as piperazole or pyridine. When R^5 , R^6 , R^7 or R^8 substituent in the ammonium group is a substituted phenyl or substituted phenylalkyl, the substituents on the phenyl and phenalkyl will generally be selected from halo, (C_1-C_8) alkyl, (C_1-C_4) alkoxy, hydroxy, nitro, trifluoromethyl, cyano, amino and (C_1-C_4) alkylthio. Such substituted phenyl groups preferably have up to two such substituents. Representative ammonium cations include ammonium, dimethylammonium, 2-ethylhexylammonium, bis(2-hydroxyethyl)ammonium, tris(2-hydroxyethyl)ammonium, dicyclohexylammonium, t-octylammonium, 2-hydroxyethylammonium, morpholinium, piperidinium, 2-phenethylammonium, 2-methylbenzylammonium, n-hexylammonium, triethylammonium, trimethylammonium, tri(n-butyl)ammonium, methoxyethylammonium, diisopropylammonium, pyridinium, dialkylammonium, pyrazolium, propargylammonium, dimethylhydrazinium, octadecylammonium, 4-dichlorophenylammonium, 4-nitrobenzylammonium, benzyltrimethylammonium, 2-hydroxyethyl-dimethyloctadecylammonium, 2-hydroxyethyldiethyloctylammonium, decyltrimethylammonium, hexyltriethylammonium and 4-methylbenzyltrimethylammonium. Among the acid addition salts are those in which the anion is an agronomically acceptable anion such as

hydrochloride, hydrobromide, sulfate, nitrate, perchlorate, acetate and oxalate.

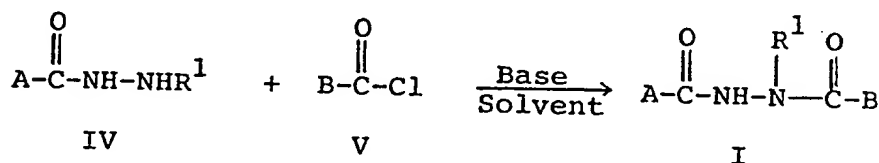
The compounds of this invention or their precursors can be prepared according to the following processes. Process A can be used when preparing compounds according to Formula I where X and X' are both oxygen.

Process A:

Step 1



Step 2

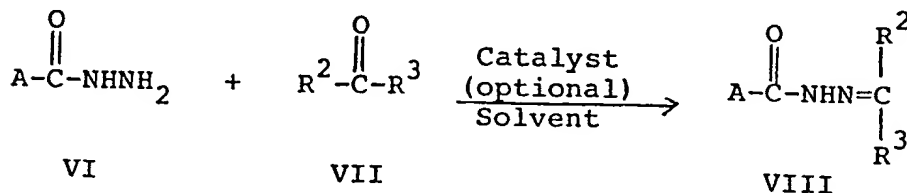


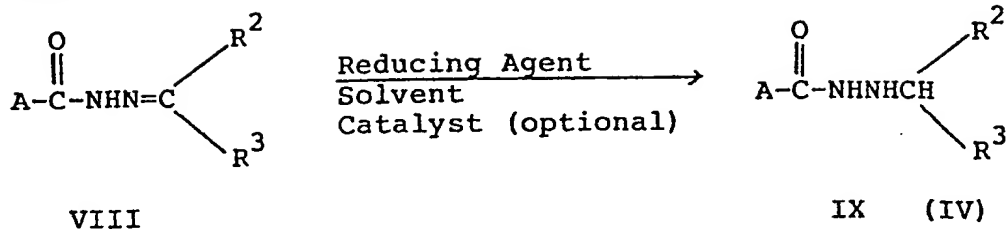
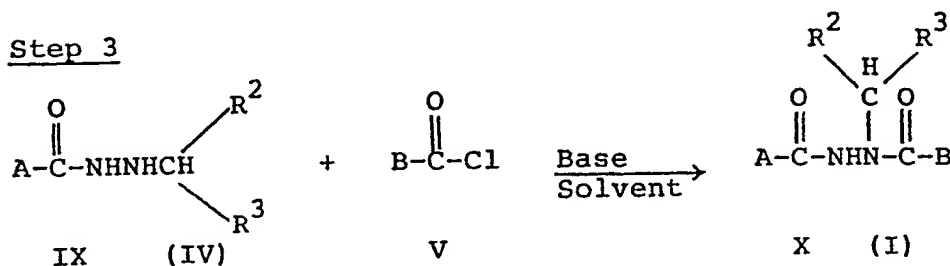
where R^1 , A and B are as defined above for Formula I and X and X' are oxygen.

Alternatively, process B can be used when preparing compounds according to Formula I where X and X' are oxygen, and R^1 , A and B are as defined above for Formula I.

Process B:

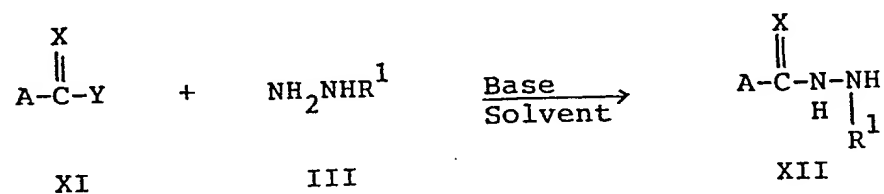
Step 1

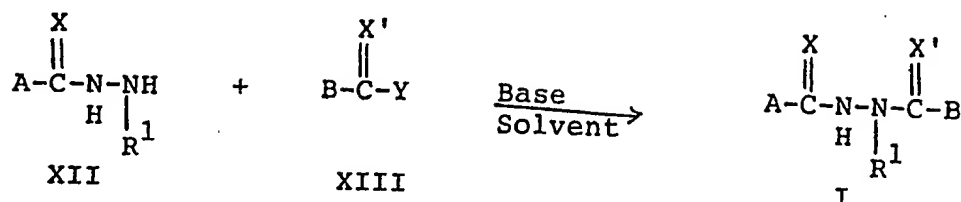


Step 2Step 3

where X and X' are oxygen, A and B are as defined above for Formula I, and R² and R³ are the same or different hydrogen or (C₂-C₉) straight or branched chain alkyl provided that R² and R³ are not both H or R² or R³ is not a straight chain alkyl group when the other (R² or R³) is hydrogen. As can be seen above, the intermediate product of Step 2, the compounds of Formula IX, corresponds to the compounds of Formula IV. In addition, the compound of Formula X corresponds to the compounds of Formula I where X and X' are oxygen.

Process C can be used when preparing compounds according to Formula I where A, B and R¹ are as defined for Formula I and one or both X and X' are sulfur.

Process C:Step 1

Step 2

wherein A, B and R¹ are as defined above for Formula I and one or both X and X' are sulfur, and Y is a good leaving group such as carboxyalkylthio (for example, carboxymethylthio -SCH₂CO₂H); alkylthio (for example, methylthio); or halo (for example, chloro).

In process A, a compound of Formula II is reacted with a monosubstituted hydrazine of Formula III or a corresponding acid addition salt such as the hydrochloride salt or the like, in the presence of a base in an inert or substantially inert solvent or mixture of solvents to afford an intermediate product of Formula IV which can be isolated or further reacted with a compound of Formula V in the presence of a base in an inert or substantially inert solvent or mixture of solvents to afford the desired product of Formula I.

Examples of the compounds of Formula II which can be used in the above processes include benzoyl chloride, 4-chlorobenzoyl chloride, 4-methylbenzoyl chloride, 3,5-dichlorobenzoyl chloride, 2-bromobenzoyl chloride and 3-cyanobenzoyl chloride.

Examples of the compounds of Formula V which can be used in the above processes include cyclohexyl-carbonyl chloride, *n*-butanoyl chloride, *n*-pentanoyl chloride, phenylacetyl chloride, 1-cyclohexenecarbonyl chloride, pivaloyl chloride, trichloroacetyl chloride and methacryloyl chloride.

The compounds of Formula II and/or Formula V are generally commercially available or can be prepared by known procedures.

Examples of the compounds of Formula III which can be used in the above processes include isopropylhydrazine, t-butylhydrazine, neopentylhydrazine, alpha-methylneopentylhydrazine, isobutylhydrazine, isopentylhydrazine and isooctylhydrazine. The compounds of Formula III are generally commercially available or can be prepared by known procedures.

Suitable solvents for use in the above processes include water; alcohols such as methanol, ethanol and isopropanol; hydrocarbons such as toluene, xylene, hexane and heptane; glyme; tetrahydrofuran; acetonitrile; pyridine; and/or haloalkanes such as methylene chloride. Mixtures of solvents can be used.

Preferred solvents are water, toluene and/or methylene chloride.

Examples of bases for use in the above processes include tertiary amines such as triethylamine; pyridine; potassium carbonate; sodium carbonate; sodium bicarbonate; sodium hydroxide; and potassium hydroxide. Preferred bases are sodium hydroxide, potassium hydroxide and triethylamine.

In Process B, a compound of Formula VI is reacted with a ketone or aldehyde of Formula VII in an inert or substantially inert solvent or mixture of solvents and optionally in the presence of a catalyst to afford an intermediate product of Formula VIII. The intermediate product of Formula VIII is then further reacted with a reducing agent in an inert or substantially inert solvent or mixture of solvents to afford a second intermediate product of Formula IX (IV) which can be isolated or further reacted with a compound of Formula V in the presence of a base in an inert or substantially inert solvent or mixture of solvents to afford the desired product of Formula X (I).

Examples of the compounds of Formula VI which can be used in the above Process B include benzoylhydrazine, 4-chlorobenzoylhydrazine, 2-methylbenzoylhydrazine, 4-methylbenzoylhydrazine, 3,5-dichlorobenzoylhydrazine and the like. The compounds of Formula VI are generally commercially available or can be prepared by known procedures.

Examples of the compounds of Formula VII which can be used in the above Process B include 1,1,1-trimethylacetaldehyde, methylethylketone and diethylketone. The compounds of Formula VII are generally commercially available or can be prepared by known procedures.

Optionally, a catalyst may be used in Step 1 of Process B. Suitable catalysts generally include organic acids such as acetic acid, trifluoroacetic acid and oxalic acid; mineral acids such as hydrochloric acid, sulfuric acid and nitric acid; arylsulfonic acids such as toluenesulfonic acid; or pyridinium toluenesulfonate. Preferred catalysts are organic acids or arylsulfonic acids. Most preferred catalysts are acetic acid and trifluoroacetic acid.

Suitable solvents for use in the above Process B, Step 1, include alcohols such as methanol, ethanol and isopropanol; hydrocarbons such as toluene and benzene; ethers such as tetrahydrofuran (THF) and glyme; and dimethylformamide. Preferred solvents are alcohols and hydrocarbons. Most preferred solvents are alcohols such as methanol and ethanol.

Examples of suitable reducing agents for use in the above Process B, Step 2, include hydrides such as sodium borohydride and derivatives thereof such as sodium cyanoborohydride, lithium aluminum hydride and derivatives thereof; or diborane. Preferred reducing agents are sodium borohydride and derivatives thereof

or lithium aluminum hydride and derivatives thereof. Most preferred as a reducing agent is sodium cyanoborohydride.

5 Optionally, in Process B, Step 2, a catalyst may be included. Examples of suitable catalysts include organic acids such as acetic acid, trifluoroacetic acid; or mineral acids such as hydrochloride acid and sulfuric acid. Preferred catalysts are organic acids and hydrochloric acid. Most preferred catalysts are
10 acetic acid, trifluoroacetic acid and hydrochloric acid.

 Suitable solvents for use in the above Process B, Step 2, include alcohols such as methanol, ethanol and isopropanol; ethers such as tetrahydrofuran (THF),
15 diethylether and glyme; or halohydrocarbons such as methylene chloride and chloroform. Preferred solvents are alcohols and most preferred are methanol and ethanol.

 Step 3 of Process B corresponds to Step 2 of
20 Process A. Consequently, those bases and solvents suitable for use in Step 2 of Process A are suitable for use in Step 3 of Process B including the preferred bases and solvents described above.

 In Process C, a compound of Formula XI is
25 reacted with a monosubstituted hydrazine of Formula III or a corresponding acid addition salt such as the hydrochloride salt in the presence of a base in an inert or substantially inert solvent or mixture of solvents to afford an intermediate compound of Formula
30 XII which can be isolated or further reacted with a compound of Formula XIII in the presence of a base in an inert or substantially inert solvent or mixture of solvents to afford the desired product of Formula I.

 Examples of the compounds of Formula XI which
35 can be used in the above Process C include 3-methyl-

methylthio-thiobenzoate, 4-chloromethylthio-thiobenzoate, 4-methyl-methylthio-thiobenzoate and carboxymethylthio-thiobenzoate.

5 Examples of the compounds of Formula XIII which can be used in the above Process C include methylthio-thiobutyrate, methylthio-thiopentanoate, methylthio-thiocyclopentanecarboxylate and methylthio-alpha-phenylthioacetate.

10 The compounds of Formula XI and/or Formula XII are generally commercially available or can be prepared by known procedures.

15 Suitable solvents for use in Process C are generally polar high-boiling solvents such as dimethylformamide (DMF); glyme; tetrahydrofuran (THF); and pyridine. The preferred solvent is pyridine.

 Suitable bases for use in Process C include tertiary amines such as triethylamine; and pyridine. The preferred base is pyridine.

20 The above processes A and B can be carried out at temperatures between about -20°C and about 100°C, preferably between about -5°C and about 50°C.

 Process C can be carried out at temperatures between about 10°C and 200°C, preferably between about 70°C and about 100°C.

25 Preparation of the compounds of the present invention by processes A, B and C is generally carried out at about atmospheric pressure although higher or lower pressures can be used if desired.

30 Substantially equimolar amounts of reactants are preferably used in processes A, B and C although higher or lower amounts can be used if desired.

35 Generally, about one equivalent of base is used per equivalent of starting material of Formula II, V, XI and/or XIII. Where the acid addition salt of the monosubstituted hydrazine of Formula III is used, one additional equivalent of base is used. For example, in

Process A, when substituents A and B are the same and a monosubstituted hydrazine is used, about two equivalents of base are used since about two equivalents of a suitably substituted benzoyl chloride of Formula II or V are employed. In Process A, when substituents A and B are different and an acid addition salt of the monosubstituted hydrazine of Formula III is used, about two equivalents of base are used in step 1 and about one equivalent of base is used in step 2.

Modifications to the above processes may be necessary to accommodate reactive functionalities of particular A and/or B substituents. Such modifications would be apparent to those skilled in the art.

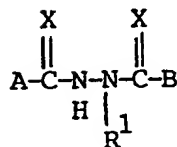
The compounds of the invention which are agronomically acceptable salts of compounds of Formula I can be prepared by reacting a metal hydroxide, a metal hydride or an amine or ammonium salt, such as a halide, hydroxide or alkoxide with a compound of Formula I having one or more hydroxy or carboxy groups or reacting a quaternary ammonium salt, such as chloride, bromide or nitrate with a metal salt of a compound of Formula I in a suitable solvent. When metal hydroxides are used as reagents, useful solvents include water; ethers such as glyme; dioxane; tetrahydrofuran; alcohols such as methanol, ethanol and isopropanol. When metal hydrides are used as reagents, useful solvents include nonhydroxylic solvents, for example, ethers such as dioxane, glyme and diethylether; tetrahydrofuran; hydrocarbons such as toluene, xylene, hexane, pentane, heptane and octane; and dimethylformamide. When amines are used as reagents, useful solvents include alcohols, such as methanol or ethanol; hydrocarbons, such as toluene, xylene and hexane; tetrahydrofuran; glyme; dioxane; or water. When ammonium salts are used as reagents,

useful solvents include water; alcohols, such as methanol or ethanol; glyme; or tetrahydrofuran. When the ammonium salt is other than a hydroxide or alkoxide, an additional base, such as potassium or sodium hydroxide, hydride, or alkoxide is generally used. The particular choice of solvent will depend on the relative solubilities of the starting materials and the resultant salts, and slurries rather than solutions of certain reagents may be used to obtain the salts. Generally, equivalent amounts of the starting reagents are used and the salt-forming reaction is carried out at about 0°C to about 100°C, preferably at about room temperature.

The acid addition salts of the invention can be prepared by reacting hydrochloric, hydrobromic, sulfuric, nitric, phosphoric, acetic, propionic, benzoic or other suitable acid with a compound of Formula I having a basic functional group in a suitable solvent. Useful solvents include water, alcohols, ethers, esters, ketones and haloalkanes. The particular choice of solvent will depend on the relative solubilities of the starting materials and the resulting salts and slurries rather than solutions of certain reagents may be used to obtain the salts. Generally, equivalent molar amounts of starting materials are used and the salt-forming reaction is carried out at from about -10°C to about 100°C, preferably at about room temperature.

The following examples are given solely to further illustrate this invention. In Table I, some N'-substituted-N-acyl-N'-alkylcarbonylhydrazines of the present invention that have been made are listed. Structures were confirmed by NMR and in some cases by IR and/or elemental analysis. Specific illustrative preparation of the compounds of Examples 1, 2, 7, 8, 10, 18 and 21 are described after Table I.

TABLE I



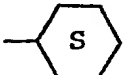
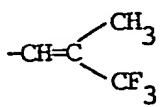
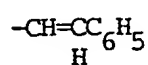
Ex. No.	X	X'	R ¹	A	B	m.p. (°C)
1	O	O	-C(CH ₃) ₃	-C ₆ H ₅	-CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	117-118
2	O	O	-C(CH ₃) ₃	-C ₆ H ₅		202-204
3	O	O	-C(CH ₃) ₃	-C ₆ H ₃ Cl ₂ -3,5	-CH ₂ CH ₂ Br	Solid
4	O	O	-C(CH ₃) ₃	-C ₆ H ₃ Cl ₂ -3,5	-CH ₂ Cl	Solid
5	O	O	-C(CH ₃) ₃	-C ₆ H ₃ Cl ₂ -3,5	-CH(CH ₃)Br	Solid
6	O	O	-C(CH ₃) ₃	-C ₆ H ₃ Cl ₂ -3,5	-CH=CH ₂	Solid
7	O	O	-C(CH ₃) ₃	-C ₆ H ₅	-C(CH ₃) ₃	217-220
8	O	O	-C(CH ₃) ₃	-C ₆ H ₅	-CH ₂ C ₆ H ₅	167-169
9	O	O	-C(CH ₃) ₃	-C ₆ H ₃ Cl ₂ -3,4	-CH ₃	119-130
10	O	O	-C(CH ₃) ₃	-C ₆ H ₅		Oil
11	O	O	-C(CH ₃) ₃	-C ₆ H ₄ Cl-4	-C(CH ₃) ₃	212-213
12	O	O	-C(CH ₃) ₃	-C ₆ H ₄ Cl-4		210
13	O	O	-C(CH ₃) ₃	-C ₆ H ₄ Cl-4	-CH ₂ C ₆ H ₅	215

TABLE I (Cont'd)

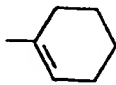





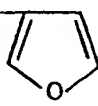

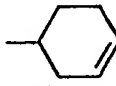
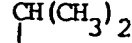
Ex. No.	X	X'	R ¹	A	B	m.p. (°C)
14	O	O	-C(CH ₃) ₃	-C ₆ H ₃ NO ₂ -2-Cl-4	-CH=CC ₆ H ₄ CF ₃ -3 H	180
15	O	O	-C(CH ₃) ₃	-C ₆ H ₃ NO ₂ -2-Cl-4	-CH=CC ₆ H ₄ CN-4 H	248
16	O	O	-C(CH ₃) ₃	-C ₆ H ₃ NO ₂ -2-Cl-4	-CH=CC ₆ H ₄ Cl-4 H	245
17	O	O	-C(CH ₃) ₃	-C ₆ H ₅		192-193
18	O	O	-C(CH ₃) ₃	-C ₆ H ₅	-C(CH ₃)=CH ₂ 	148-152
19	O	O	-C(CH ₃) ₃	-C ₆ H ₅	 - 	175-177
20	O	O	-C(CH ₃) ₃	-C ₆ H ₃ Cl ₂ -3,4		157-158
21	O	O	-C(CH ₃) ₃	-C ₆ H ₄ Cl-4		188-192
22	O	O	-C(CH ₃) ₃	-C ₆ H ₅	-CH=C-  H	Solid
23	O	O	-C(CH ₃) ₃	-C ₆ H ₅	 -CHCO ₂ CH ₂ CH ₃	Low melting solid
24	O	O	-C(CH ₃) ₃	-C ₆ H ₃ (CH ₃) ₂ -2,3		188
25	O	O	-C(CH ₃) ₃	-C ₆ H ₃ (CH ₃) ₂ -2,3	 -CH- C ₆ H ₄ Cl-4	160-163

TABLE I (Cont'd)

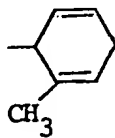
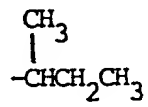
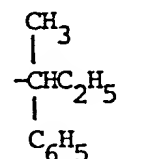
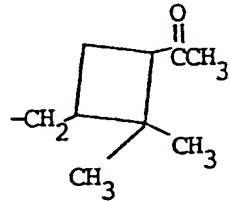
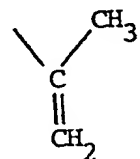
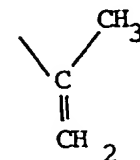
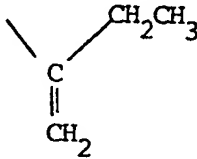
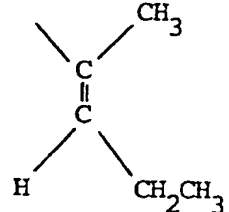
Ex. No.	X	X'	R ¹	A	B	m.p. (°C)
26	O	O	-C(CH ₃) ₃	-C ₆ H ₅		
27	O	O	-C(CH ₃) ₃	-C ₆ H ₅	-C≡C-C ₆ H ₅	146-147
28	O	O	-C(CH ₃) ₃	-C ₆ H ₅		148-150
29	O	O	-C(CH ₃) ₃	-C ₆ H ₅		165-166
30	O	O	-C(CH ₃) ₃	-C ₆ H ₅		low melting solid
31	O	O	-C(CH ₃) ₃	-C ₆ H ₅	-CH=CHCH ₂ CH ₃	
32	O	O	-C(CH ₃) ₃	-C ₆ H ₅	-CH ₂ CH ₂ CH=CH ₂	
33	O	O	-C(CH ₃) ₃	-C ₆ H ₅	-CH ₂ CH ₂ CH ₂ CO ₂ CH ₃	Oil
34	O	O	-C(CH ₃) ₃	-C ₆ H ₅	-CH ₂ OCH ₃	117-118
35	O	O	-C(CH ₃) ₃	-C ₆ H ₃ (CH ₃) _{2-2,3}		115-118
36	O	O	-C(CH ₃) ₃	-C ₆ H ₄ CH ₂ CH ₃ - ⁴		108-118

TABLE I (Cont'd)

Ex. No.	X	X'	R ¹	A	B	m.p. (°C)
37	O	O	-C(CH ₃) ₃	-C ₆ H ₃ (CH ₃) ₂ -2,3	-CH(CH ₃) ₂	143-144
38	O	O	-C(CH ₃) ₃	-C ₆ H ₃ (CH ₃) ₂ -2,3	-C(CH ₃) ₃	175-181
39	O	O	-C(CH ₃) ₃	-C ₆ H ₃ (CH ₃) ₂ -2,3		118-122
40	O	O	-C(CH ₃) ₃	-C ₆ H ₃ (CH ₃) ₂ -2,3		140-143

EXAMPLE NO. 1 - Preparation of N'-t-butyl-N-benzoyl-N'-n-pentanecarbonylhydrazine

To a stirred suspension of t-butylhydrazine hydrochloride (1 g, 0.008 M) in toluene (30 ml) at room temperature was added dropwise a 50% aqueous solution of sodium hydroxide (0.64 g, 0.008 M). After 15 min., the reaction mixture was cooled to 5°C and a solution of benzoyl chloride (1.12 g, 0.008 M) in toluene (5 ml) and a solution of aqueous 50% sodium hydroxide (0.64 g, 0.008 M) were added dropwise simultaneously from separate addition funnels while maintaining the temperature at or below 10°C. Following the addition, the reaction mixture was warmed to room temperature and stirred for 1 hr. The reaction was diluted with hexane and the solid N'-t-butyl-N-benzoylhydrazine (IV) was isolated by filtration.

To a stirred solution of the monobenzoylet compound (1.4 g, 0.0073 M) in toluene (30 ml) at 5°C, were added dropwise simultaneously from separate addition funnels, solutions of hexanoyl chloride (1 g, 0.0073 M) in toluene (5 ml) and aqueous 50% sodium hydroxide solution (0.58 g, 0.0073 M) while maintaining the temperature below 10°C. Following the addition, the reaction mixture was warmed to room temperature and stirred for 1 hr. The mixture was then diluted with hexane and the solid product isolated by filtration. The product was washed with water and hexane and dried. The crude product was recrystallized from ether-methanol to afford N'-t-butyl-N-benzoyl-N'-n-pentane-carbonylhydrazine as a white powder. m.p. 117-118°C.

15 EXAMPLE NO. 2 - Preparation of N'-t-butyl-N-benzoyl-N'-cyclohexanecarbonylhydrazine

To a stirred suspension of t-butylhydrazine hydrochloride (1 g, 0.008 M) in toluene (30 ml) at room temperature was added dropwise a 50% aqueous solution of sodium hydroxide (0.64 g, 0.008 M). After 15 min., the reaction mixture was cooled to 5°C and a solution of benzoyl chloride (1.12 g, 0.008 M) in toluene (5 ml) and a solution of aqueous 50% sodium hydroxide (0.64 g, 0.008 M) were added dropwise simultaneously from separate addition funnels while maintaining the temperature at or below 10°C. Following the addition, the reaction mixture was warmed to room temperature and stirred for 1 hr. The reaction was diluted with hexane and the solid N'-t-butyl-N-benzoylhydrazine was isolated by filtration.

30 To a stirred solution of the monobenzoylet compound (1.4 g, 0.0073 M) in toluene (30 ml) at 5°C, were added dropwise simultaneously from separate addition funnels, solutions of cyclohexanecarbonyl

chloride (1.1 g, 0.0073 M) in toluene (5 ml) and aqueous 50% sodium hydroxide solution (0.58 g, 0.0073 M) while maintaining the temperature below 10°C. Following the addition, the reaction mixture was warmed to room temperature and stirred for 1 hr. The mixture was then diluted with hexane and the solid product isolated by filtration. The product was washed with water and hexane and dried. The crude product was recrystallized from ether-methanol to afford N'-t-butyl-N-benzoyl-N'-cyclohexanecarbonylhydrazine as a white powder. m.p. 202-204°C.

EXAMPLE NO. 7 - Preparation of N'-t-butyl-N-benzoyl-N'-pivaloylhydrazine

To a stirred suspension of t-butylhydrazine hydrochloride (2 g, 0.016 M) in toluene (50 ml) at room temperature was added dropwise a 50% aqueous solution of sodium hydroxide (1.28 gm, 0.016 M). After 15 min., the reaction mixture was cooled to 5°C and a solution of benzoyl chloride (2.3 g, 0.017 M) in toluene (5 ml) and a solution of aqueous 50% sodium hydroxide (1.36 g, 0.017 M) were added dropwise simultaneously from separate addition funnels while maintaining the temperature at or below 10°C. Following the addition, the reaction mixture was warmed to room temperature and stirred for 1 hr. The reaction mixture was diluted with hexane and the solid N'-t-butyl-N-benzoylhydrazine was isolated by filtration.

To a stirred solution of the monobenzoylated compound (2 g, 0.010 M) in pyridine (15 ml) was added pivaloyl chloride (1.8 g, 0.015 M) and a catalytic amount of 4-dimethylamino pyridine. The mixture was heated to 60°C and stirred for approximately 1 hr., cooled and diluted with methylene chloride. The organic layer was washed with 10% HCl (3 x 25 ml) and

water (50 ml), dried over magnesium sulfate and the solvent removed under vacuum. The solid product was recrystallized from methanol-ether to afford N'-t-butyl-N-benzoyl-N'-pivaloylhydrazine in 60% yield as a white solid. m.p. 217-220°C.

EXAMPLE No. 8 - Preparation of N'-t-butyl-N-benzoyl-N'-phenylacetylhydrazine

To a stirred suspension of t-butylhydrazine hydrochloride (1 g, 0.008 M) in toluene (30 ml) at room temperature was added dropwise a 50% aqueous solution of sodium hydroxide (0.64 g, 0.008 M). After 15 min., the reaction mixture was cooled to 5°C and a solution of benzoyl chloride (1.12 g, 0.008 M) in toluene (5 ml) and a solution of aqueous 50% sodium hydroxide (0.64 g, 0.008 M) were added dropwise simultaneously from separate addition funnels while maintaining the temperature at or below 10°C. Following the addition, the reaction mixture was warmed to room temperature and stirred for 1 hr. The reaction was diluted with hexane and the solid N'-t-butyl-N-benzoylhydrazine was isolated by filtration.

To a stirred solution of the monobenzoylated compound (1.5 g, 0.0078 M) in toluene (30 ml) at 5°C, were added dropwise simultaneously from separate addition funnels, solutions of phenylacetyl chloride (1.2 g, 0.008 M) in toluene (5 ml) and aqueous 50% sodium hydroxide solution (0.63 g, 0.0078 M) while maintaining the temperature below 10°C. Following the addition, the reaction mixture was warmed to room temperature and stirred for 1 hr. The mixture was then diluted with hexane and the solid product isolated by filtration. The product was washed with water and hexane and dried. The crude product was recrystallized from ether-methanol to afford N'-t-butyl-N-benzoyl-N'-

phenylacetylhydrazine as a white powder. m.p. 167-169°C.

EXAMPLE NO. 10 - Preparation of N'-t-butyl-N-benzoyl-N'-(beta-trifluoromethylcrotonyl)hydrazine

5 N'-t-butyl-N-benzoylhydrazine (1.0 g) in 2 ml
toluene was added dropwise to a solution of beta-
trifluoromethyl-crotonyl chloride (prepared by addition
of oxalyl chloride (1.3 g) to a solution of 1.5 g beta-
trifluoromethyl-crotonic acid in 5 ml toluene at 23°C).
10 After 30 min. at 23°C, the reaction mixture was
partitioned between saturated aqueous sodium
bicarbonate (20 ml) and ether (20 ml). The ether layer
was evaporated under reduced pressure to about 10 ml
and the excess hydrazine was removed by filtration.
15 The filtrate was evaporated to give N'-t-butyl-N-
benzoyl-N'-(beta-trifluoromethyl-crotonyl)hydrazine as
a colorless oil.

EXAMPLE NO. 18 - Preparation of N'-t-butyl-N-benzoyl-N'-methacryloylhydrazine

20 N'-t-butyl-N-benzoylhydrazine (0.9 g) suspended
in 10 ml toluene and 1 ml H₂O containing 0.3 g 50%
sodium hydroxide was treated with 1.2 g of methacryloyl
chloride at 23°C. After 18 hours, 5 ml of hexane was
added and N'-t-butyl-N-benzoyl-N'-methacryloylhydrazine
25 was collected by filtration. m.p. 148-152°C.

EXAMPLE NO. 21 - Preparation of N'-t-butyl-N'-cyclo-
butanecarbonyl-N-(4-chlorobenzoyl)hydrazine

To a stirred solution of N'-t-butyl-N-(4-chloro-
benzoyl)hydrazine (2.0 g, 8.8 mmole) in toluene (35 ml)
30 at 5°C was added cyclobutanecarboxylic acid chloride
(1.25 g, 10.5 mmole) in one portion. To the above
mixture was dropwise added 50% NaOH solution (0.85 g,

10.6 mmole). After addition, the ice water bath was removed and the reaction mixture was stirred at room temperature overnight.

5 The mixture was diluted with hexane (30 ml) and H₂O (30 ml) and stirred for another 30 min. The solid product was collected by suction-filtration and washed with H₂O (100 ml) and hexane (100 ml) to yield 1.5 g of N'-t-butyl-N'-cyclobutanecarbonyl-N-(4-chlorobenzoyl)-hydrazine.

10 By following substantially the procedures in Processes A, B and C as exemplified above by the preparation of the compounds of Examples 1, 2, 7, 8, 10, 18 and 21, the compounds of Formula I can be prepared and the compounds of the remaining Examples
15 were prepared.

As previously noted, the compounds of the present invention exhibit excellent pesticidal activity and are selective against insects of the orders Lepidoptera and Coleoptera.

20 In general, for the control of insects in agriculture, horticulture and forestry, a dosage corresponding to from about 10 grams to about 10 kilograms of the active substance per hectare may be used and from about 100 grams to about 5 kilograms per
25 hectare of the active substance is preferred. The exact amount of dosage for a given situation can be determined by routine testing and depends on a variety of factors, for example, the substance used, the kind of pest, the formulation used, the state of the crop
30 infested with the pest and the prevailing weather conditions. The term "insecticidal" as employed in the specification and claims of this application is to be construed as any means which adversely affects the existence or growth of the target insects. Such means
35 can comprise a complete killing action, eradication,

arresting in growth, inhibition, reducing in number or any combination thereof. The terms "control" and "combat" as employed in the specification and claims of this application is to be construed as including an "insecticidal" action and the protection of plants from insect damage. By "insecticidally effective amount" is meant that dosage of active substance sufficient to exert insect "control".

The compounds of the present invention, for practical applications, can be utilized in the form of compositions or formulations. Examples of the preparation of compositions and formulations can be found in the American Chemical Society publication "Pesticidal Formulation Research," (1969), Advances in Chemistry Series No. 86, written by Wade Van Valkenburg; and the Marcel Dekker, Inc. publication "Pesticide Formulations," (1973), edited by Wade Van Valkenburg. In these compositions and formulations, the active substance is mixed with conventional inert agronomically acceptable (i.e., plant compatible and/or pesticidally inert) diluents or extenders such as solid carrier material or liquid carrier material, of the type usable in conventional compositions or formulations. By agronomically acceptable carrier is meant any substance which can be used to dissolve, disperse or diffuse the active ingredient in the composition without impairing the active ingredient's effectiveness and which by itself has no significant detrimental effect on the soil, equipment, desirable plants or agronomic environment. If desired, adjuvants such as surfactants, stabilizers, antifoam agents and antidrift agents may also be added.

Examples of compositions and formulations according to the invention are aqueous solutions and dispersions, oily solutions and oil dispersions,

pastes, dusting powders, wettable powders, emulsifiable concentrates, flowables, granules, baits, invert emulsions, aerosol compositions and fumigating candles.

5 Wettable powders, pastes, flowables and emulsifiable concentrates are concentrated preparations which are diluted with water before or during use.

10 Baits are preparations generally comprising a food or other substance attractive to the target pest, that includes at least one lethal or non-lethal toxicant. Lethal toxicants kill the pest upon ingesting the bait with non-lethal toxicants change the behavior, feeding habits and physiology of the pest for the purpose of control.

15 The invert emulsions are mainly used for aerial application, where large areas are treated with a comparatively small amount of preparation. The invert emulsion may be prepared in the spraying apparatus shortly before, or even during, the spraying operation by emulsifying water in an oil solution or an oil
20 dispersion of the active substance.

 Compositions and formulations can be prepared in a known manner, for instance by extending the active compounds with conventional dispersible liquid diluent carriers and/or dispersible solid carriers optionally
25 with the use of carrier vehicle assistants, e.g., conventional surface-active agents, including emulsifying agents and/or dispersing agents, whereby, for example, in the case where water is used as diluent, organic solvents may be added as auxiliary
30 solvents. The following may be chiefly considered for use as conventional carrier vehicles for this purpose: aerosol propellants which are gaseous at normal temperatures and pressures, such as halogenated hydrocarbons, e.g., dichlorodifluoromethane and
35 trifluorochloromethane, as well as butane, propane,

nitrogen and carbon dioxide; inert dispersible liquid diluent carriers, including inert organic solvents, such as aromatic hydrocarbons (e.g., benzene, toluene, xylene, alkyl naphthalenes, etc.), halogenated, especially chlorinated, aromatic hydrocarbons (e.g., chlorobenzenes, etc.), cycloalkanes (e.g., cyclohexane, etc.), paraffins (e.g., petroleum or mineral oil fractions), chlorinated aliphatic hydrocarbons (e.g., methylene chloride, chloroethylenes, etc.), vegetable oils (e.g., soybean oil, cottonseed oil, corn oil, etc.), alcohols (e.g., methanol, ethanol, propanol, butanol, glycol, etc.) as well as ethers and esters thereof (e.g., glycol monomethyl ether), amines (e.g., ethanolamine), amides (e.g., dimethyl formamide), sulfoxides (e.g., dimethyl sulfoxide), acetonitrile, ketones (e.g., acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, isophorone), and/or water; solid carriers including ground natural minerals, such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals, such as highly-dispersed silicic acid, alumina and silicates; solid carriers for granules include crushed and fractionated natural rocks such as calcite, marble, pumice, sepiolite and dolomite, as well as synthetic granules of inorganic and organic meals, and granules of organic material such as sawdust, coconut shells, corn cobs and tobacco stalks. The following may be chiefly considered for use as conventional carrier vehicle assistants: emulsifying agents, such as cationic and/or nonionic and/or anionic emulsifying agents (e.g., polyethylene oxide esters of fatty acids, polyethylene oxide ethers of fatty alcohols, alkyl sulfates, alkyl sulfonates, aryl sulfonates, albumin hydrolysates and especially alkyl arylpolyglycol ethers, magnesium stearate, sodium

oleate); and/or dispersing agents, such as lignin, sulfite waste liquors, methyl cellulose.

5 Adhesives such as carboxymethylcellulose and natural and synthetic polymers in the form of powders, granules or latices, such as gum arabic, polyvinyl alcohol and polyvinyl acetate, can be used in the formulations.

10 If desired, it is possible to use colorants in compositions and formulations containing compounds of the present invention such as inorganic pigments, for example, iron oxide, titanium oxide and Prussian Blue, and organic dyestuffs, such as alizarin dyestuffs, azo dyestuffs and metal phthalocyanine dyestuffs, and trace nutrients such as salts of iron, manganese, boron, 15 copper, cobalt, molybdenum and zinc.

 The active compounds of the present invention may be employed alone or in the form of mixtures with one another and/or with such solid and/or liquid dispersible carrier vehicles and/or with other known 20 compatible active agents, especially plant protection agents, such as other insecticides, arthropodicides, nematocides, fungicides, bactericides, rodenticides, herbicides, fertilizers, growth-regulating agents and synergists if desired, or in the form of particular 25 dosage preparations for specific application made therefrom, such as solutions, emulsions, suspensions, powders, pastes, and granules which are thus ready for use.

30 As concerns commercially marketed preparations, these generally contemplate carrier composition mixtures in which the active compound is present in an amount substantially between about 0.1% and 99% by weight, and preferably between about 1% and 75% by 35 weight, of the mixture. Carrier composition mixtures suitable for direct application or field application

generally contemplate those in which the active compound is used in an amount substantially between about 0.0001% and 5%, preferably between about 0.001% and 3%, by weight of the mixture. Thus the present invention contemplates overall formulations and compositions which comprise mixtures of a conventional dispersible carrier such as (1) a dispersible inert finely divided carrier solid, and/or (2) a dispersible carrier liquid such as an inert organic solvent and/or water, preferably including a surface-active effective amount of a carrier vehicle assistant (e.g., a surface-active agent, such as an emulsifying agent and/or a dispersing agent), and an amount of the active compound generally between about 0.0001% and about 99% by weight of the composition, preferably between about 0.001% and about 90% by weight of the composition and more preferably between about 0.01% and about 75% by weight of the composition which is effective for the purpose in question.

The active compounds can be applied as sprays by conventional methods, such as conventional high-gallonage hydraulic sprays, low gallonage sprays, ultra-low-volume sprays, airblast spray, aerial sprays and dusts. If low volume applications are desired, a solution of the compound is usually used. In ultra-low-volume applications, a liquid composition containing the active compound is usually applied as a spray (e.g., mist) by means of atomizing equipment in finely divided form (average particle size of from about 50 to about 100 microns or less) using airplane crop spraying techniques. Typically only a few liters per hectare are needed and often amounts up to about 15 to 1000 g/hectare, preferably about 40 to 600 g/hectare are sufficient. With ultra-low-volume, it is possible to use highly concentrated liquid compositions with said

liquid carrier vehicles containing from about 20 to about 95% by weight of the active compound.

Furthermore, the present invention contemplates methods of selectively killing, combating or
5 controlling pests, which comprises contacting insects with a correspondingly combative of at least one active compound of the invention alone or together with a carrier vehicle (composition or formulation) as noted above. The term "contacting" as employed in the
10 specification and claims of this application is to be construed as applying to at least one of (a) such insects and (b) the corresponding habitat thereof (i.e., the locus to be protected, for example, to a growing crop or an area where a crop is to be grown)
15 the active compound of this invention alone or as a constituent of a composition or formulation. The formulations or compositions are applied in the usual manner, for instance by spraying, atomizing, vaporizing, scattering, dusting, watering, squirting,
20 sprinkling, pouring, fumigating, dry dressing, moist dressing, wet dressing, slurry dressing, encrusting or otherwise disseminating.

It will be realized, of course, that the concentration of the particular active compound
25 utilized in admixture with the carrier vehicle will depend upon such factors as the type of equipment employed, method of application, area to be treated, types of pests to be controlled and degree of infestation. Therefore, in special cases it is
30 possible to go above or below the aforementioned concentration ranges.

Granular preparations are produced for example, by taking up the active substance in a solvent and by using the resulting solution, as the case may be in the
35 presence of a binder, to impregnate a granular carrier

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material, such as porous granules (for example, pumice and attaclay) or chopped tobacco stems or the like.

5 A granular preparation (frequently termed a "pellet") may alternatively be produced by compressing the active substance together with powdered minerals in the presence of lubricants and binders and by disintegrating and straining the composite to the desired grain size.

10 Dusts are obtainable by intimately mixing the active substance with an inert solid carrier material in a concentration of from about 1 to about 50% by weight. Examples of suitable solid carrier materials are talc, kaolin, pipe clay, diatomaceous earth, dolomite, gypsum, chalk, bentonite, attapulgitite and
15 colloidal SiO_2 or mixtures of these and similar substances. Alternatively organic carrier materials such as, for example, ground walnut shells may be used.

Wettable powders and flowables are conveniently produced by mixing from about 10 to about 99 parts by
20 weight of a solid inert carrier such, for example, as the aforementioned carrier materials with from about 1 to about 80 parts by weight of active substance optionally dissolved in a volatile solvent such as acetone, from about 1 to about 5 parts by weight of
25 dispersing agent such, for example, as the ligno-sulfonates or alkyl-naphthalene sulfonates known for this purpose and preferably also from about 0.5 to about 5 parts by weight of wetting agent, such as fatty alcohol sulfates, or alkylarylsulfonates of fatty acid
30 condensation products. In the case of flowables, a liquid inert carrier such as water also included.

To produce emulsifiable concentrates the active compound is dissolved or finely divided in a suitable solvent which preferably is poorly miscible with water, emulsifier being added to the resulting solution.
35

Examples of suitable solvents are xylene, toluene, high-boiling aromatic petroleum distillates, for example solvent naphtha, distilled tar oil and mixtures of these liquids. Examples of suitable emulsifiers are alkylphenoxypolyglycol ethers, polyoxyethylene sorbitan esters of fatty acids or polyoxyethylene sorbitol esters of fatty acids. The concentration of the active compound in these emulsifiable concentrates is not restricted within narrow limits and may vary between about 2% and about 50% by weight depending upon toxicant solubility. A suitable liquid highly concentrated primary composition other than an emulsifiable concentrate is a solution of the active substance in a liquid which is readily miscible with water, for example, acetone, to which solution a dispersant and, as the case may be, a wetting agent are added. When such a primary composition is diluted with water shortly before or during the spraying operation an aqueous dispersion of the active substance is obtained.

An aerosol preparation according to the invention is obtained in the usual manner by incorporating the active substance or a solution thereof in a suitable solvent in a volatile liquid suitable for use as a propellant such, for example, as a mixture of chlorine and fluorine derivatives of methane and ethane.

Fumigating candles or fumigating powders, i.e., preparations which when burning are capable of emitting a pesticidal smoke, are obtained by taking up the active substance in a combustible mixture which may, for example, comprise a sugar or a wood, preferably in the ground form, as a fuel, a substance to sustain combustion such, for example, as ammonium nitrate or potassium chlorate, and furthermore a substance for

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retarding combustion, for example kaolin, bentonite and/or colloidal silicic acid.

5 A bait preparation comprises a food or other substance attractive to pests, a carrier, the toxicant and may optionally include other substances commonly used in preparations of this kind, such as, a preservative to inhibit bacterial and fungal growth, a waterproofing agent to prevent disintegration under wet conditions and dyes or colorants as described above.

10 In addition to the aforementioned ingredients, the preparations according to the invention may also contain other substances commonly used in preparations of this kind.

15 For example, a lubricant, such as calcium stearate or magnesium stearate, may be added to a wettable powder or to a mixture to be granulated. Furthermore, there may, for example, be added "adhesives" such as polyvinylalcohol cellulose derivatives or other colloidal materials, such as
20 casein, to improve the adherence of this pesticide to the surface to be protected.

Representative preparation of compositions and formulations including the compounds of the present invention are set forth below as Examples A through I
25 by way of illustration but not limitation.

Example A

Granular

	<u>Ingredient</u>	<u>%/wt.</u>
	Toxicant and toxicant impurities	0.25
30	Triton X-305 (binder)	0.25
	(Octylphenyl-3-ethylene oxide ethanol)	
	Agisorb 24/48 (diluent)	99.50

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Preparation: The toxicant and Triton X-305 are dissolved into methylene chloride and the mixture is added to the Agsorb with continuous mixing. The methylene chloride is then allowed to evaporate.

5

Example BDust

<u>Ingredient</u>	<u>%/wt.</u>
Toxicant and toxicant impurities	1.0
Talc 99.0	

10

Preparation: Toxicant is dissolved in excess acetone and the mixture is impregnated onto the talc. The acetone is then permitted to evaporate.

Example CWettable Powder

15

<u>Ingredient</u>	<u>%/wt.</u>
Toxicant and toxicant impurities	31.3
Duponal WA Dry (wetter)	2.0
(Sodium lauryl sulfate)	
Reax 45A (dispersant)	5.0
(Sodium lignin sulfonate)	
Barden clay (diluent)	31.7
HiSil 233 (diluent)	30.0
(Sodium silica)	

20

25

Preparation: The toxicant, optionally dissolved in a volatile solvent, is absorbed onto the Barden clay and HiSil carriers. The Duponal and Reax are then added and the entire dry mixture blended until homogenous. The composition is then micronized to a fine particle size.

Example DEmulsifiable Concentrate

	<u>Ingredient</u>	<u>%/wt.</u>
	Toxicant and toxicant impurities	15.0
	Sponto 232T (emulsifier)	6.0
	(Anionic and nonionic blend of the following surfactants: calcium dodecyl benzene sulfonate; and ethoxylated alkylphenol)	
0	Sponto 234T (emulsifier)	4.0
	(Anionic and nonionic blend of the following surfactants: calcium dodecyl benzene sulfonate; and ethoxylated alkylphenol)	
5	Cyclohexanone (solvent)	22.5
	Tenneco 500-100 (solvent)	52.5
	(Aromatic solvent mixture principally comprising xylene, cumene and ethyl benzene having a boiling point range of 290-345°F)	
10		

Preparation: All ingredients are mixed together with continuous agitation until a homogeneous clear solution is obtained.

Example E

25

Aerosol

<u>Ingredient</u>	<u>%/wt.</u>
Toxicant and toxicant impurities	0.5
Freon 12	99.5

30 Preparation: The components are mixed and packaged under pressure in a suitable container equipped with a release spray valve.

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Example FFumigating Candle or Fumigating Powder

	<u>Ingredient</u>	<u>%/wt.</u>
	Toxicant and toxicant impurities	1.0
5	Wood dust	96.0
	Starch	3.0

Preparation: Toxicant, wood dust, and starch are blended together and then molded into a candle using a small amount of water to activate the starch.

10

Example GBaitMethod A

	<u>Ingredient</u>	<u>%/wt.</u>
	Toxicant and toxicant impurities	1.00
15	Wheat Bran (carrier and attractant)	89.95
	Corn Syrup (attractant)	7.00
	Corn Oil (attractant)	2.00
	Kathon 4200 ((3-isothiazolone) preservative)	0.05

20

Preparation: The corn oil and corn syrup are added to the wheat bran with adequate mixing. The toxicant and Kathon are premixed with excess acetone and this solution is added to the wheat bran base with continued mixing. The acetone is then permitted to

25

evaporate.

Method B

	<u>Ingredient</u>	<u>%/wt.</u>
	Toxicant and toxicant impurities	0.06
	Granulated Sugar (carrier and attractant)	99.94

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Example HPellet

Same as Example G, Method A, with this addition:
 the bait composition is formed into 1/4" diameter by
 3/8" long pellets using a suitable die and press
 apparatus.

Example IFlowable

	<u>Ingredient</u>	<u>%/wt.</u>
10	Toxicant and toxicant impurities	31.3
	Duponal WA Dry (wetter)	2.0
	(Sodium lauryl sulfate)	
	Reax 45A (dispersant)	5.0
	(Sodium lignin sulfonate)	
15	HiSil 233 (diluent)	30.0
	(Sodium silica)	
	Kelzan (thickener)	0.5
	(Xanthan gum)	
	Water	31.2

Preparation: The toxicant is absorbed onto the
 HiSil carrier. The Duponal and Reax are then added and
 the entire dry mixture blended until homogeneous. The
 composition is then micronized to a fine particle size.
 The resulting powder is suspended in water and the
 Kelzan added.

Compositions and formulations according to the
 present invention may also include known pesticidal
 compounds. This expands the spectrum of activity of
 the preparations and may give rise to synergism.

The following known insecticidal, fungicidal and
 acaricidal compounds are suitable for use in such a
 combined preparation.

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Insecticides such as:

Chlorinated hydrocarbons, for example, 2,2-bis(p-chlorophenyl)-1,1,1-trichloroethane and hexachloroepoxyoctahydrodimethanonaphthalene;

5 Carbamates, for example, N-methyl-1-naphthylcarbamates;

Dinitrophenols, for example, 2-methyl-4,6-dinitrophenol and 2-(2-butyl)-4,6-dinitrophenyl-3,3-dimethylacrylate;

10 Organic phosphorus compounds, such as dimethyl-2-methoxy-3-carbonyl-1-methylvinyl phosphate, O,O-diethyl-O-p-nitrophenylphosphorothioate; N-monomethylamide of O,O-dimethyldithiophosphorylacetic acid;

15 Diphenylsulfides, for example, p-chlorobenzyl or p-chlorophenyl sulfide and 2,4,4',5-tetrachlorodiphenylsulfide;

Diphenylsulfonates, for example, p-chlorophenylbenzenesulfonate;

20 Methylcarbinols, for example, 4,4-dichloro-1-trichloromethylbenzhydrol;

Quinoxaline compounds, such as methylquinoxaline dithiocarbonate;

Amidines such as N'-(4-chloro-2-methylphenyl) N,N-dimethylformamidine;

25 Pyrethroids such as Allethrin;

Biologicals such as Bacillus thuringiensis preparations;

Organic tin compounds such as tricyclohexyltin hydroxide;

Synergists such as piperonyl butoxide.

30 Fungicides such as:

Organic mercury compounds, for example, phenylmercuryacetate and methylmercurycyanoguanide;

Organic tin compounds, for example, triphenyltin hydroxide and triphenyltin acetate;
Alkylenebisdithiocarbamates, for example, zinc ethylene-bisdithiocarbamate and manganese
5 ethylenebisdithiocarbamate; and
2,4-dinitro-6-(2-octyl-phenylcrotonate), 1-bis(dimethylamino)phosphoryl-3-phenyl-5-amino-1,2,4-triazole, 6-methylquinoxaline-2,3-dithiocarbonate, 1,4-dithioanthraquinone-2,3-
10 dicarbonitrile, N-trichloromethylthio-phthalimide, N-trichloromethylthiotetrahydro-phthalimide, N-(1,1,2,2-tetrachloroethylthio)-tetrahydrophthalimide, N-dichlorofluoromethylthio-N-phenyl-N'-dimethylsulfonyldiamide and
15 tetrachloroisophthalonitrile.

Biological Activity

It has been found by biological evaluation that compounds of the invention have pesticidal activity and are capable of controlling larvae and adult forms of
20 pests, especially insects from the orders Lepidoptera and Coleoptera. One skilled in the art will know how to determine the activity of a given compound against a given insect and the dosage required to obtain general or selective insecticidal effects.

25 As previously noted, the compounds of the invention are particularly suitable for controlling plant-destructive insects in crops of cultivated plants, such as, but not limited to, cotton, vegetables, corn and other cereals; forestry, such as,
30 but not limited to, birch, spruce, pine and fir; and ornamental plants, flowers and trees. Compounds of the invention are also particularly suitable for controlling insects destructive to stored commodities such as seeds; fruit crops, such as, but not limited

to, fruit and citrus trees and raspberry bushes; and turf, such as, but not limited to, lawns and sod.

In evaluating the pesticidal activity of the compounds of this invention, the following test procedures were employed.

A test solution containing 600 parts per million (ppm) was made by dissolving the test compound in a solvent (acetone:methanol, 1:1), adding water to give an acetone:methanol:water system of 5:5:90 and then a surfactant. A 1:1 mixture of an alkylaryl polyether-alcohol (sold as Triton X-155) and a modified phthalic glycerol alkyl resin (sold as Triton B-1956) was utilized at the equivalent of 1 ounce per 100 gal. of test solution as a surfactant.

Initial evaluations were made on one or more of the following pests.

Code

<u>Symbol</u>	<u>Common Name</u>	<u>Latin Name</u>
SAW	Southern Armyworm	<u>Spodoptera eridania</u>
MBB	Mexican Bean Beetle	<u>Epilachna varivestis</u>

For the foliar bean beetle and armyworm tests, individual bean (Phaseolus limensis var. Woods' Prolific) leaves are placed on moistened pieces of filter paper in Petri dishes. The leaves are then sprayed with the test solution using a rotating turntable and allowed to dry. The dishes are infested with 10 third instar larvae of Southern armyworm or Mexican bean beetle. The dishes are then covered.

The percent mortality for the bean beetle and armyworm evaluations are determined 96 hours after treatment. Evaluations are based on a scale of 0-100% in which 0 equals no activity and 100 equals total kill.

The rotating turntable consists of a fixed,

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continuously operating spray nozzle under which targets are rotated at a fixed speed and distance. When the target is a Petri dish (such as for the armyworm), the distance from the nozzle is 15 inches. The nozzle is located 8 inches from the rotating shaft. The targets on individual platforms revolve around the shaft at 1 revolution per 20 seconds but only a brief portion of this time occurs in the spray path. Targets pass only once under the nozzle and then are removed to drying hoods.

The nozzle used is a 1/4 JCO Spraying Systems (Wheaton, Illinois) air atomizing nozzle equipped with a No. 2850 fluid cap and No. 70 air cap. At the 10 psig air pressure used and with liquid siphon feed 0.5 GPH (gallons per hour) are delivered in a round spray pattern with a 21° spray angle. Targets are misted with spray droplets to the point that the droplets coalesce to form a uniform thin film insufficient to drown test organisms.

All treatments are maintained at 75-80°F under continuous fluorescent light in a well-ventilated room.

For soil treatment (systemic) trials, a portion of the 600 ppm test solution is diluted to 150 ppm. Ten (10) ml of the 150 ppm test solution is pipetted into soil (approximately 200 g of standard greenhouse soil) in a 3-inch pot containing a lima bean seedling. This results in a soil concentration of approximately 8 ppm. Treated plants are maintained under existing greenhouse conditions for one week. Two bean leaves are removed and placed individually on moist filter paper in Petri dishes. One leaf is infested with 10 third instar larvae of Mexican bean beetle. The other leaf is infested with 10 third instar larvae of Southern armyworm. The dishes are then covered and held for 3 days at which time the percent control

preclude insect starvation.

The results of the initial insecticidal evaluations are given in Table II.

5 Armyworm and bean beetle spray (foliar) results
are 96 hour observations. Soil treatment results are
72 hour observations. At the discretion of the
experimenter, particular evaluations were held for 144
hour observations. If, after 144 hours, there was a
change in the percent control, it is shown in
10 parentheses.

TABLE II

Biological Evaluations

<u>Example No.</u>	<u>Foliar Application</u>		<u>Soil Application</u>	
	<u>Test Species</u>		<u>Test Species</u>	
	<u>SAW</u>	<u>MBB</u>	<u>MBB</u>	<u>SAW</u>
1	10	40	-- ^a	--
2	100	0	0	20
3	20 ^b	100 ^b	--	--
4	0 ^b	0 ^b	--	--
5	0 ^b	0 ^b	--	--
6	0 ^b	0 ^b	--	--
7	100	100	60 (100)	100
8	90	50	40 (100)	0 (20)
9	0	0	0	0
10	0	10	0	0
11	80	0 ^b	--	--
12	0	20	0	0
13	80	80	0	0
14	0	30	0	0
15	0	40	20	0
16	0	0	0	0
17	100	0	0	100
18	100	100	60 (100)	90
19	0	0	0	0
20	0	10	40 (20)	0
21	0	100	0	0
22	10 ^b	0 ^b	--	--

^a Not tested^b 48 hour results

TABLE II (Cont'd)Biological Evaluations

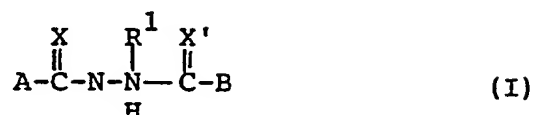
<u>Example No.</u>	<u>Foliar Application</u> <u>Test Species</u>		<u>Soil Application</u> <u>Test Species</u>	
	<u>SAW</u>	<u>MBB</u>	<u>MBB</u>	<u>SAW</u>
23	0	30	-	-
24	80	0	-	-
25	30	30	-	-
26	100	40	-	-
27	100	10	-	-
28	0	100	-	-
29	100	30	-	-
30	100	30	-	-
31	100	20	-	-
32	100	60	-	-
33	100	40	-	-
34	100	20	-	-
35	100	0	-	-
36	100	40	-	-
37	0	70	-	-
38	0	20	-	-
39	100	0	-	-
40			-	-

In its mechanical aspects therefore a process of the invention for improving the commercial value and/or profitability of vendible crops from plants whose growth is affected or likely to be affected by insects comprises (1) charging to a container, fumigation device or mechanical dissemination device an insecticidal composition of the invention as hereinbefore described (2) using the container, fumigator or mechanical dissemination device to apply the insecticidal composition, in the form of granules, dust, smoke, vapour or surfactant-containing liquid preparation to growing plants or to a growth medium where the plants are growing or are to be grown, or to the insects themselves, (3) controlling the dose of the active ingredient during this application step so that the rate of application of active insecticidal compound is sufficient to combat the insects but is insufficient to cause an unacceptably adverse effect on the crop plants growing or to be grown in the treated area.

The following words are trademarks which may or may not be registered in some or all of the designated states: Triton, Agsorb, Duponal, Reax, Hisil, Sponto, Tenneco, Kathon and Kelzan.

CLAIMS:

1. An insecticidally active compound which is a compound of the formula



wherein

- 5 X and X' are the same or different O, S or NR;
 R¹ is unsubstituted branched (C₃-C₁₀)alkyl or
 straight chain (C₁-C₄)alkyl substituted with
 one or two of the same or different
 (C₃-C₆)cycloalkyl;
- 10 A is unsubstituted or substituted naphthyl where
 the substituents can be from one to three of
 the same or different halo; cyano; nitro;
 hydroxy; (C₁-C₄)alkoxy; (C₁-C₄)alkyl; carboxy;
 (C₁-C₄)alkoxy-carbonyl; (C₁-C₄)alkanoyloxy or
 15 NH₂, NHZ or -NZZ';
- unsubstituted or substituted phenyl where the
 substituents can be from one to five of the
 same or different halo; nitro; cyano; hydroxy;
 (C₁-C₆)alkyl; halo-(C₁-C₆)alkyl; cyano-
 20 (C₁-C₆)alkyl; (C₁-C₆)alkoxy; halo-(C₁-C₆)-
 alkoxy; (C₁-C₆)alkoxy-(C₁-C₆)alkyl having
 independently the stated number of carbon
 atoms in each alkyl group; (C₁-C₆)alkoxy-
 (C₁-C₆)alkoxy having independently the stated
 25 number of carbon atoms in each alkyl group;
 -OCO₂R group; (C₂-C₆)alkenyl optionally
 substituted with halo, cyano, (C₁-C₄)alkyl,
 (C₁-C₄)alkoxy, halo-(C₁-C₄)alkoxy or (C₁-C₄)-

alkylthio; carboxy; $\text{-RCO}_2\text{R}'$ group; -COR ;
 halo- $(\text{C}_1\text{-C}_6)$ alkyl-carbonyl; cyano- $(\text{C}_1\text{-C}_6)$ -
 alkyl-carbonyl; nitro- $(\text{C}_1\text{-C}_6)$ alkyl-carbonyl;
 $(\text{C}_1\text{-C}_6)$ alkoxy-carbonyl; halo- $(\text{C}_1\text{-C}_6)$ -
 5 alkoxy-carbonyl; -OCOR group; $\text{-NRR}'$ group;
 amino substituted with hydroxy, $(\text{C}_1\text{-C}_4)$ alkoxy
 or $(\text{C}_1\text{-C}_4)$ alkylthio groups; phenylamino;
 diphenylamino; $\text{-CONRR}'$ group; $\text{-OCONRR}'$ group;
 $\text{-NRCOR}'$ group; $\text{-NRCO}_2\text{R}'$ group; $\text{-N(COR)COR}'$
 10 group; $\text{-OCONRCOR}'$ group; sulfhydryl; halothio;
 $(\text{C}_1\text{-C}_6)$ alkylthio; halo- $(\text{C}_1\text{-C}_6)$ alkylthio; -SOR
 group; $\text{-SO}_2\text{R}$ group; phenylsulfonyl; $\text{-OSO}_2\text{R}$
 group; halo- $(\text{C}_1\text{-C}_6)$ alkylsulfonyloxy; $\text{-SO}_2\text{NRR}'$
 group; $\text{-NRSOR}'$ group; $\text{-NRSO}_2\text{R}'$ group; -CSR
 15 group; CS_2R group; $\text{-NRCSR}'$ group; -SCOR group;
 unsubstituted or substituted phenyl having one
 to three of the same or different halo, cyano,
 nitro, hydroxy $(\text{C}_1\text{-C}_4)$ alkyl, $(\text{C}_1\text{-C}_4)$ alkoxy,
 carboxy, $(\text{C}_1\text{-C}_4)$ alkoxy-carbonyl, $(\text{C}_1\text{-C}_4)$ -
 20 alkanoyloxy, NH_2 , NHZ or $\text{-NZZ}'$; phenoxy where
 the phenyl ring is unsubstituted or
 substituted with one to three of the same or
 different halo, cyano, nitro, hydroxy,
 $(\text{C}_1\text{-C}_4)$ alkyl, $(\text{C}_1\text{-C}_4)$ alkoxy, carboxy, $(\text{C}_1\text{-C}_4)$ -
 25 alkoxy-carbonyl, $(\text{C}_1\text{-C}_4)$ alkanoyloxy, NH_2 , NHZ
 or $\text{-NZZ}'$; phenylthio where the phenyl ring is
 unsubstituted or substituted with one to three
 of the same or different halo, cyano, nitro,
 hydroxy, $(\text{C}_1\text{-C}_4)$ alkyl, $(\text{C}_1\text{-C}_4)$ alkoxy, carboxy,
 30 $(\text{C}_1\text{-C}_4)$ alkoxy-carbonyl, $(\text{C}_1\text{-C}_4)$ alkanoyloxy,
 NH_2 , NHZ or $\text{-NZZ}'$; or when two adjacent
 positions on the phenyl ring are substituted
 with alkoxy groups, these groups may be joined
 to form, together with the carbon atoms to
 35 which they are both attached, a 5- or 6-

membered dioxolano or dioxano heterocyclic ring;

5 B is unsubstituted or substituted (C_1-C_{10})alkyl having as the optional substituent(s) one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4)alkoxy, halo-(C_1-C_4)-alkoxy, carboxy, (C_1-C_4)alkoxycarbonyl, (C_1-C_4)alkanoyloxy, phenyl, NH_2 , NHZ or -NZZ'.

10 unsubstituted or substituted (C_3-C_8)cycloalkyl or unsubstituted or substituted (C_3-C_8)cycloalkyl(C_1-C_4)alkyl, having as the optional substituent(s) one to four of the same or differet halo, cyano, nitro, hydroxy, (C_1-C_4)-alkyl, halo-(C_1-C_4)alkyl, (C_1-C_4)alkoxy, halo-15 (C_1-C_4)alkoxy, carboxy, (C_1-C_4)alkanoyl, (C_1-C_4)alkoxy-carbonyl, (C_1-C_4)alkanoyloxy, NH_2 , NHZ or -NZZ';

20 unsubstituted or substituted (C_2-C_8)alkenyl or unsubstituted or substituted (C_3-C_8)alkadienyl having, as the optional substituent(s), a furyl, thienyl or pyridyl group or one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4)alkyl, (C_3-C_6)cycloalkyl, halo-(C_1-C_4)alkyl, (C_1-C_4)alkoxy, halo-25 (C_1-C_4)alkoxy, carboxy, (C_1-C_4)alkoxy-carbonyl, (C_1-C_4)alkanoyloxy, NH_2 , NHZ or -NZZ';

30 unsubstituted or substituted (C_3-C_8)cycloalkenyl or unsubstituted or substituted (C_3-C_8)cycloalkadienyl having as the optional substituent(s), one to four of the same or different halo, cyano, nitro, hydroxy,

(C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo-(C₁-C₄)alkoxy, carboxy, (C₁-C₄)-alkoxy-carbonyl, (C₁-C₄)alkanoyloxy, NH₂, NHZ or -NZZ';

unsubstituted or substituted (C₂-C₈)alkynyl having, as optional substituent(s), one to four of the same or different halo, cyano, nitro, hydroxy, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo-(C₁-C₄)alkoxy, carboxy, (C₁-C₄)alkoxy-carbonyl, (C₁-C₄)alkanoyloxy, phenyl, NH₂, NHZ or -NZZ';

phenalkyl having one to four carbon atoms in the alkyl group and wherein the alkyl group is unsubstituted or substituted with one to three of the same or different halo, cyano, hydroxy, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, (C₁-C₄)-alkoxy-carbonyl, NH₂, NHZ or -NZZ', and the phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, cyano-(C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo-(C₁-C₄)alkoxy, carboxy, (C₁-C₄)alkoxy-carbonyl, (C₁-C₄)alkanoyloxy, (C₂-C₆)alkenyl, halo-(C₂-C₆)alkenyl, (C₂-C₆)-alkynyl, NH₂, NHZ or -NZZ'; or

phenalkenyl having two to six carbon atoms in the alkenyl group and the alkenyl group is unsubstituted or substituted with one to three of the same or different halo, cyano, hydroxy, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)-alkoxy, halo-(C₁-C₄)alkoxy, (C₁-C₄)-alkoxy-carbonyl, NH₂, NHZ or -NZZ', and the

phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo-(C₁-C₄)alkoxy, carboxy, (C₁-C₄)alkoxy-carbonyl, (C₁-C₄)alkanoyloxy or NH₂, NHZ or -NZZ';

where R and R' are hydrogen or (C₁-C₆)alkyl; Z and Z' are (C₁-C₄)alkyl; "amino" means NRR'; or an agronomically acceptable salt thereof; except for such a compound in which X and X' are O, R¹ is t-butyl, A is unsubstituted phenyl and B is unsubstituted methyl or unsubstituted ethyl.

2. A compound according to claim 1 which is a compound wherein

X and X' are O or S; and/or

R¹ is unsubstituted branched (C₃-C₈)alkyl or a straight chain (C₁-C₄)alkyl substituted with one or two of the same or different (C₃-C₄)-cycloalkyl; and/or

A is unsubstituted naphthyl; or

unsubstituted or substituted phenyl where the substituents can be from one to three of the same or different halo; nitro, cyano; (C₁-C₄)alkyl; halo-(C₁-C₄)alkyl; cyano-(C₁-C₄)alkyl, (C₁-C₄)alkoxy; (C₁-C₄)alkoxy-(C₁-C₄)alkyl; -COD; carboxy; (C₁-C₄)alkoxy-carbonyl; (C₁-C₄)alkanoyloxy; NH₂, NHZ or -NZZ'; (C₁-C₄)alkylthio; -CSD; -CS₂D; -SCOD; unsubstituted or substituted phenyl having one to two of the same or different halo, nitro, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, carboxy, (C₁-C₄)alkoxy-carbonyl, (C₁-C₄)alkanoyloxy,

NH₂, NHZ or -NZZ'; or when two adjacent positions on the phenyl ring are substituted with alkoxy groups, these groups are joined to form, together with the carbon atoms to which they are attached, a 5- or 6-membered dioxolano or dioxano heterocyclic ring; and/or

B is unsubstituted or substituted (C₁-C₈)alkyl having as the optional substituent(s) one to three of the same or different halo, cyano, (C₁-C₄)alkoxy, phenyl, (C₁-C₄)alkoxy-carbonyl or halo-(C₁-C₄)alkoxy;

unsubstituted or substituted (C₃-C₆)cycloalkyl or unsubstituted or substituted (C₃-C₅)cycloalkyl-(C₁-C₄)alkyl, having as the optional substituent(s) one or two of the same or different halo, (C₁-C₄)alkyl, halo-(C₁-C₄)-alkyl, (C₁-C₄)alkoxy, (C₁-C₄)alkanoyl or (C₁-C₄)haloalkoxy;

unsubstituted or substituted (C₂-C₆)alkenyl having as the optional substituent(s) a furyl or one to three of the same or different (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy or halo-(C₁-C₄)alkoxy;

unsubstituted or substituted (C₃-C₆)cycloalkenyl having as the optional substituent(s) one or two of the same or different halo, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy or halo-(C₁-C₄)alkoxy;

unsubstituted or phenyl substituted alkynyl;

phenalkyl having one or two carbon atoms in the alkyl group and the alkyl group is unsubstituted or substituted with one or two of the same or different halo, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy or halo-(C₁-C₄)alkoxy and the phenyl ring is unsubstituted or substituted with one or two of the same or different halo, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy or halo-(C₁-C₄)alkoxy; or

phenalkenyl having two or three carbon atoms in the alkenyl group and the alkenyl group is unsubstituted or substituted with halo, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)-alkoxy or halo-(C₁-C₄)alkoxy and the phenyl ring is unsubstituted or substituted with one or two of the same or different halo, (C₁-C₄)-alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy or halo-(C₁-C₄)alkoxy; or an

agronomically acceptable salt thereof; wherein D is hydrogen or (C₁-C₄)alkyl and Z and Z' are (C₁-C₄)alkyl.

3. A compound according to claim 2 which is a compound wherein

X and X' are O or S; and/or
R¹ is branched (C₃-C₈)alkyl; and/or
A is unsubstituted naphthyl; or
unsubstituted or substituted phenyl having one to three of the same or different halo, nitro, cyano, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, cyano-(C₁-C₄)alkyl, (C₁-C₄)alkoxy, -COD, (C₁-C₄)-alkoxy-carbonyl, (C₁-C₄)alkanoyloxy, or

unsubstituted or substituted phenyl having one or two of the same or different halo, nitro, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, carboxy, (C₁-C₄)alkoxy-carbonyl, (C₁-C₄)alkanoyloxy, NH₂, NHZ or -NZZ'; and/or

B is unsubstituted or substituted (C₁-C₆)alkyl having one to three of the same or different halo, cyano, (C₁-C₄)alkoxy, phenyl, (C₁-C₃)alkoxy-carbonyl or halo-(C₁-C₄)alkoxy;

0 unsubstituted or substituted (C₃-C₆)cycloalkyl or unsubstituted or substituted (C₃-C₆)cycloalkyl-(C₁-C₄)alkyl where the optional substituent is halo, (C₁-C₄)alkyl, (C₁-C₄)alkanoyl, (C₁-C₄)alkoxy or halo-(C₁-C₄)alkoxy;

.5 unsubstituted or substituted (C₂-C₆)alkenyl having one or two of the same or different (C₁-C₄)alkyl, (C₁-C₄)alkoxy or halo-(C₁-C₄)alkoxy;

20 unsubstituted or substituted (C₄-C₆)cycloalkenyl where the substituent is halo, (C₁-C₄)alkyl, (C₁-C₄)alkoxy or halo-(C₁-C₄)alkoxy; or

unsubstituted or phenyl-substituted alkynyl;
or an

25 agronomically acceptable salt thereof.

4. A compound according to claim 3 which is a compound wherein

X and X' are O; and/or

- R^1 is branched (C_4 - C_7)alkyl; and/or
A is unsubstituted, monosubstituted, 2,3-disubstituted or 2,4-disubstituted phenyl
where the substituents can be the same or
different halo, (C_1 - C_4)alkyl, (C_1 - C_4)alkoxy,
or halo-(C_1 - C_4)alkyl; and/or
B is unsubstituted or substituted (C_1 - C_6)alkyl
having one to three of the same or different
halo, phenyl or cyano;
- unsubstituted (C_4 - C_6)cycloalkyl;
- unsubstituted or substituted (C_2 - C_5)alkenyl
having as the optional substituent(s) one or
two of the same or different (C_1 - C_4)alkyl;
- unsubstituted (C_4 - C_6)cycloalkenyl; or
- phenalkyl having one or two carbon atoms in
alkyl group and the phenyl ring is
unsubstituted or substituted with one or two
of the same or different halo, (C_1 - C_4)alkyl,
or (C_1 - C_4)alkoxy;
- or an agronomically acceptable salt thereof.

5. A compound according to claim 4 which is a compound wherein

- X and X' are O; and/or
 R^1 is t-butyl, neopentyl (2,2-dimethylpropyl) or
1,2,2-trimethylpropyl; and/or
A is unsubstituted or monosubstituted phenyl
where the substituent can be chloro, fluoro,
bromo, iodo, methyl, ethyl, methoxy or
trifluoromethyl; and/or

B is unsubstituted or substituted (C_1-C_4)alkyl having as the optional substituent(s) one to three of the same or different, phenyl, chloro, fluoro or bromo;

unsubstituted (C_4-C_6)cycloalkyl;

unsubstituted (C_4-C_6)cycloalkenyl; or

phenalkyl having one to two carbon atoms in the alkyl group and the phenyl ring is unsubstituted or substituted with one or two of the same or different chloro, fluoro, bromo, iodo, methyl, ethyl, methoxy or trifluoromethyl; or an agronomically acceptable salt thereof.

6. A compound according to claim 3 which is a compound wherein

X and X' are O;

R¹ is t-butyl; and

A is phenyl and B is cyclohexyl, benzyl, 1-cyclohexenyl, 2-methylcyclohexadi-2,5-enyl, phenylethynyl, 1-methylpropyl, 2-methyl-1-phenylbutyl, 3-acetyl-2,2-dimethylcyclobutyl-methyl, 1-butenyl, 3-butenyl, 3-carbomethoxy-propyl or methoxymethyl; or

A is 3,5-dichlorophenyl and B is 2-bromoethyl; or

A is 4-chlorophenyl and B is cyclobutyl; or

A is 2,3-dimethylphenyl and B is 1-methylethenyl or 1-ethylethenyl; or

A is 4-ethylphenyl and B is 1-methylethenyl.

7. An insecticidal composition comprising an agronomically acceptable diluent or carrier and an

insecticidal compound as claimed in any of claims 1 to 6.

8. A composition according to claim 7 containing the insecticidal compound in an amount of from 0.0001, preferably 0.001, to 99% by weight.

9. A composition according to claim 7 containing the insecticidal compound in an amount of from 0.01 to 99% by weight.

10. A composition according to any of claims 7 to 9 in the form of a wettable powder, a flowable, a dust, a granule, a bait or an emulsifiable concentrate.

11. A method of controlling insects which comprises contacting said insects with insecticidal compound according to any of claims 1 to 6, optionally in a composition according to any of claims 7 to 9.

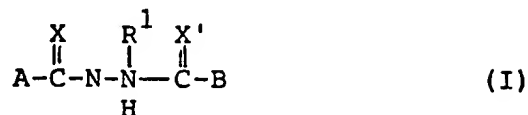
12. A method according to claim 11 which comprises applying the compound at a rate of from about 10 grams to about 10 kilograms per hectare, to growing plants or to an area where plants are to be grown.

13. A method according to claim 12 wherein the rate of application is 100 grams to 5 kilograms of the compound per hectare.

14. A method according to claim 13 of controlling insects from the order Lepidoptera or Coleoptera.

CLAIMS: AT

1. An insecticidally active composition which comprises a compound of the formula



wherein

X and X' are the same or different O, S or NR;
 R¹ is unsubstituted branched (C₃-C₁₀)alkyl or straight chain (C₁-C₄)alkyl substituted with one or two of the same or different (C₃-C₆)cycloalkyl;
 A is unsubstituted or substituted naphthyl where the substituents can be from one to three of the same or different halo; cyano; nitro; hydroxy; (C₁-C₄)alkoxy; (C₁-C₄)alkyl; carboxy; (C₁-C₄)alkoxy-carbonyl; (C₁-C₄)alkanoyloxy or NH₂, NHZ or -NZZ';

unsubstituted or substituted phenyl where the substituents can be from one to five of the same or different halo; nitro; cyano; hydroxy; (C₁-C₆)alkyl; halo-(C₁-C₆)alkyl; cyano-(C₁-C₆)alkyl; (C₁-C₆)alkoxy; halo-(C₁-C₆)-alkoxy; (C₁-C₆)alkoxy-(C₁-C₆)alkyl having independently the stated number of carbon atoms in each alkyl group; (C₁-C₆)alkoxy-(C₁-C₆)alkoxy having independently the stated number of carbon atoms in each alkyl group; -OCO₂R group; (C₂-C₆)alkenyl optionally substituted with halo, cyano, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo-(C₁-C₄)alkoxy or (C₁-C₄)-

alkylthio; carboxy; $\text{-RCO}_2\text{R}'$ group; -COR ;
 halo- $(\text{C}_1\text{-C}_6)$ alkyl-carbonyl; cyano- $(\text{C}_1\text{-C}_6)$ -
 alkyl-carbonyl; nitro- $(\text{C}_1\text{-C}_6)$ alkyl-carbonyl;
 $(\text{C}_1\text{-C}_6)$ alkoxy-carbonyl; halo- $(\text{C}_1\text{-C}_6)$ -
 alkoxy-carbonyl; -OCOR group; $\text{-NRR}'$ group;
 amino substituted with hydroxy, $(\text{C}_1\text{-C}_4)$ alkoxy
 or $(\text{C}_1\text{-C}_4)$ alkylthio groups; phenylamino;
 diphenylamino; $\text{-CONRR}'$ group; $\text{-OCONRR}'$ group;
 $\text{-NRCOR}'$ group; $\text{-NRCO}_2\text{R}'$ group; $\text{-N(COR)COR}'$
 group; $\text{-OCONRCOR}'$ group; sulfhydryl; halothio;
 $(\text{C}_1\text{-C}_6)$ alkylthio; halo- $(\text{C}_1\text{-C}_6)$ alkylthio; -SOR
 group; $\text{-SO}_2\text{R}$ group; phenylsulfonyl; $\text{-OSO}_2\text{R}$
 group; halo- $(\text{C}_1\text{-C}_6)$ alkylsulfonyloxy; $\text{-SO}_2\text{NRR}'$
 group; $\text{-NRSOR}'$ group; $\text{-NRSO}_2\text{R}'$ group; -CSR
 group; CS_2R group; $\text{-NRCSR}'$ group; -SCOR group;
 unsubstituted or substituted phenyl having one
 to three of the same or different halo, cyano,
 nitro, hydroxy $(\text{C}_1\text{-C}_4)$ alkyl, $(\text{C}_1\text{-C}_4)$ alkoxy,
 carboxy, $(\text{C}_1\text{-C}_4)$ alkoxy-carbonyl, $(\text{C}_1\text{-C}_4)$ -
 alkanoyloxy, NH_2 , NHZ or $\text{-NZZ}'$; phenoxy where
 the phenyl ring is unsubstituted or
 substituted with one to three of the same or
 different halo, cyano, nitro, hydroxy,
 $(\text{C}_1\text{-C}_4)$ alkyl, $(\text{C}_1\text{-C}_4)$ alkoxy, carboxy, $(\text{C}_1\text{-C}_4)$ -
 alkoxy-carbonyl, $(\text{C}_1\text{-C}_4)$ alkanoyloxy, NH_2 , NHZ
 or $\text{-NZZ}'$; phenylthio where the phenyl ring is
 unsubstituted or substituted with one to three
 of the same or different halo, cyano, nitro,
 hydroxy, $(\text{C}_1\text{-C}_4)$ alkyl, $(\text{C}_1\text{-C}_4)$ alkoxy, carboxy,
 $(\text{C}_1\text{-C}_4)$ alkoxy-carbonyl, $(\text{C}_1\text{-C}_4)$ alkanoyloxy,
 NH_2 , NHZ or $\text{-NZZ}'$; or when two adjacent
 positions on the phenyl ring are substituted
 with alkoxy groups, these groups may be joined
 to form, together with the carbon atoms to
 which they are both attached, a 5- or 6-

membered dioxolano or dioxano heterocyclic ring;

B is unsubstituted or substituted (C_1-C_{10})alkyl having as the optional substituent(s) one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4)alkoxy, halo- (C_1-C_4) -alkoxy, carboxy, (C_1-C_4)alkoxycarbonyl, (C_1-C_4)alkanoyloxy, phenyl, NH_2 , NHZ or -NZZ'.

unsubstituted or substituted (C_3-C_8)cycloalkyl or unsubstituted or substituted (C_3-C_8)cycloalkyl(C_1-C_4)alkyl, having as the optional substituent(s) one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4)alkyl, halo- (C_1-C_4) alkyl, (C_1-C_4)alkoxy, halo- (C_1-C_4) alkoxy, carboxy, (C_1-C_4)alkanoyl, (C_1-C_4)alkoxy-carbonyl, (C_1-C_4)alkanoyloxy, NH_2 , NHZ or -NZZ';

unsubstituted or substituted (C_2-C_8)alkenyl or unsubstituted or substituted (C_3-C_8)alkadienyl having, as the optional substituent(s), a furyl, thienyl or pyridyl group or one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4)alkyl, (C_3-C_6)cycloalkyl, halo- (C_1-C_4) alkyl, (C_1-C_4)alkoxy, halo- (C_1-C_4) alkoxy, carboxy, (C_1-C_4)alkoxy-carbonyl, (C_1-C_4)alkanoyloxy, NH_2 , NHZ or -NZZ';

unsubstituted or substituted (C_3-C_8)cycloalkenyl or unsubstituted or substituted (C_3-C_8)cycloalkadienyl having as the optional substituent(s), one to four of the same or different halo, cyano, nitro, hydroxy,

(C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo-(C₁-C₄)alkoxy, carboxy, (C₁-C₄)-alkoxy-carbonyl, (C₁-C₄)alkanoyloxy, NH₂, NHZ or -NZZ';

unsubstituted or substituted (C₂-C₈)alkynyl having, as optional substituent(s), one to four of the same or different halo, cyano, nitro, hydroxy, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo-(C₁-C₄)alkoxy, carboxy, (C₁-C₄)alkoxy-carbonyl, (C₁-C₄)alkanoyloxy, phenyl, NH₂, NHZ or -NZZ';

phenalkyl having one to four carbon atoms in the alkyl group and wherein the alkyl group is unsubstituted or substituted with one to three of the same or different halo, cyano, hydroxy, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, (C₁-C₄)-alkoxy-carbonyl, NH₂, NHZ or -NZZ', and the phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, cyano-(C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo-(C₁-C₄)alkoxy, carboxy, (C₁-C₄)alkoxy-carbonyl, (C₁-C₄)alkanoyloxy, (C₂-C₆)alkenyl, halo-(C₂-C₆)alkenyl, (C₂-C₆)-alkynyl, NH₂, NHZ or -NZZ'; or

phenalkenyl having two to six carbon atoms in the alkenyl group and the alkenyl group is unsubstituted or substituted with one to three of the same or different halo, cyano, hydroxy, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)-alkoxy, halo-(C₁-C₄)alkoxy, (C₁-C₄)-alkoxy-carbonyl, NH₂, NHZ or -NZZ', and the

phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo-(C₁-C₄)alkoxy, carboxy, (C₁-C₄)alkoxy-carbonyl, (C₁-C₄)alkanoyloxy or NH₂, NHZ or -NZZ';

where R and R' are hydrogen or (C₁-C₆)alkyl; Z and Z' are (C₁-C₄)alkyl; "amino" means NRR'; or an agronomically acceptable salt thereof; except for such a compound in which X and X' are O, R¹ is t-butyl, A is unsubstituted phenyl and B is unsubstituted methyl or unsubstituted ethyl;

together with agronomically acceptable diluent or carrier.

2. A composition according to claim 1 wherein X and X' are O or S; and/or R¹ is unsubstituted branched (C₃-C₈)alkyl or a straight chain (C₁-C₄)alkyl substituted with one or two of the same or different (C₃-C₄)-cycloalkyl; and/or A is unsubstituted naphthyl; or

unsubstituted or substituted phenyl where the substituents can be from one to three of the same or different halo; nitro, cyano; (C₁-C₄)-alkyl; halo-(C₁-C₄)alkyl; cyano-(C₁-C₄)alkyl, (C₁-C₄)alkoxy; (C₁-C₄)alkoxy-(C₁-C₄)alkyl; -COD; carboxy; (C₁-C₄)alkoxy-carbonyl; (C₁-C₄)alkanoyloxy; NH₂, NHZ or -NZZ'; (C₁-C₄)alkylthio; -CSD; -CS₂D; -SCOD; unsubstituted or substituted phenyl having one to two of the same or different halo, nitro, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, carboxy, (C₁-C₄)alkoxy-carbonyl, (C₁-C₄)alkanoyloxy,

NH₂, NHZ or -NZZ'; or when two adjacent positions on the phenyl ring are substituted with alkoxy groups, these groups are joined to form, together with the carbon atoms to which they are attached, a 5- or 6-membered dioxolano or dioxano heterocyclic ring; and/or

B is unsubstituted or substituted (C₁-C₈)alkyl having as the optional substituent(s) one to three of the same or different halo, cyano, (C₁-C₄)alkoxy, phenyl, (C₁-C₄)alkoxy-carbonyl or halo-(C₁-C₄)alkoxy;

unsubstituted or substituted (C₃-C₆)cycloalkyl or unsubstituted or substituted (C₃-C₅)cycloalkyl-(C₁-C₄)alkyl, having as the optional substituent(s) one or two of the same or different halo, (C₁-C₄)alkyl, halo-(C₁-C₄)-alkyl, (C₁-C₄)alkoxy, (C₁-C₄)alkanoyl or (C₁-C₄)haloalkoxy;

unsubstituted or substituted (C₂-C₆)alkenyl having as the optional substituent(s) a furyl or one to three of the same or different (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy or halo-(C₁-C₄)alkoxy;

unsubstituted or substituted (C₃-C₆)cycloalkenyl having as the optional substituent(s) one or two of the same or different halo, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy or halo-(C₁-C₄)alkoxy;

unsubstituted or phenyl substituted alkynyl;

phenalkyl having one or two carbon atoms in the alkyl group and the alkyl group is unsubstituted or substituted with one or two of the same or different halo, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy or halo-(C₁-C₄)alkoxy and the phenyl ring is unsubstituted or substituted with one or two of the same or different halo, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy or halo-(C₁-C₄)alkoxy; or

phenalkenyl having two or three carbon atoms in the alkenyl group and the alkenyl group is unsubstituted or substituted with halo, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy or halo-(C₁-C₄)alkoxy and the phenyl ring is unsubstituted or substituted with one or two of the same or different halo, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy or halo-(C₁-C₄)alkoxy;

wherein D is hydrogen or (C₁-C₄)alkyl and Z and Z' are (C₁-C₄)alkyl.

3. A composition according to claim 2 wherein X and X' are O or S; and/or R¹ is branched (C₃-C₈)alkyl; and/or A is unsubstituted naphthyl; or unsubstituted or substituted phenyl having one to three of the same or different halo, nitro, cyano, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, cyano-(C₁-C₄)alkyl, (C₁-C₄)alkoxy, -COD, (C₁-C₄)alkoxy-carbonyl, (C₁-C₄)alkanoyloxy, or

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unsubstituted or substituted phenyl having one or two of the same or different halo, nitro, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, carboxy, (C₁-C₄)alkoxy-carbonyl, (C₁-C₄)alkanoyloxy, NH₂, NHZ or -NZZ'; and/or

B is unsubstituted or substituted (C₁-C₆)alkyl having one to three of the same or different halo, cyano, (C₁-C₄)alkoxy, phenyl, (C₁-C₃)alkoxy-carbonyl or halo-(C₁-C₄)alkoxy;

unsubstituted or substituted (C₃-C₆)cycloalkyl or unsubstituted or substituted (C₃-C₆)cycloalkyl-(C₁-C₄)alkyl where the optional substituent is halo, (C₁-C₄)alkyl, (C₁-C₄)alkanoyl, (C₁-C₄)alkoxy or halo-(C₁-C₄)alkoxy;

unsubstituted or substituted (C₂-C₆)alkenyl having one or two of the same or different (C₁-C₄)alkyl, (C₁-C₄)alkoxy or halo-(C₁-C₄)alkoxy;

unsubstituted or substituted (C₄-C₆)cycloalkenyl where the substituent is halo, (C₁-C₄)alkyl, (C₁-C₄)alkoxy or halo-(C₁-C₄)alkoxy; or

unsubstituted or phenyl-substituted alkynyl.

4. A composition according to claim 3 wherein X and X' are O; and/or

R^1 is branched (C_4 - C_7)alkyl; and/or
A is unsubstituted, monosubstituted, 2,3-disubstituted or 2,4-disubstituted phenyl where the substituents can be the same or different halo, (C_1 - C_4)alkyl, (C_1 - C_4)alkoxy, or halo-(C_1 - C_4)alkyl; and/or
B is unsubstituted or substituted (C_1 - C_6)alkyl having one to three of the same or different halo, phenyl or cyano;

unsubstituted (C_4 - C_6)cycloalkyl;

unsubstituted or substituted (C_2 - C_5)alkenyl having as the optional substituent(s) one or two of the same or different (C_1 - C_4)alkyl;

unsubstituted (C_4 - C_6)cycloalkenyl; or

phenalkyl having one or two carbon atoms in alkyl group and the phenyl ring is unsubstituted or substituted with one or two of the same or different halo, (C_1 - C_4)alkyl, or (C_1 - C_4)alkoxy.

5. A composition according to claim 4 wherein
X and X' are O; and/or
 R^1 is t-butyl, neopentyl (2,2-dimethylpropyl) or 1,2,2-trimethylpropyl; and/or
A is unsubstituted or monosubstituted phenyl where the substituent can be chloro, fluoro, bromo, iodo, methyl, ethyl, methoxy or trifluoromethyl; and/or

B is unsubstituted or substituted (C_1-C_4)alkyl having as the optional substituent(s) one to three of the same or different, phenyl, chloro, fluoro or bromo;

unsubstituted (C_4-C_6)cycloalkyl;

unsubstituted (C_4-C_6)cycloalkenyl; or

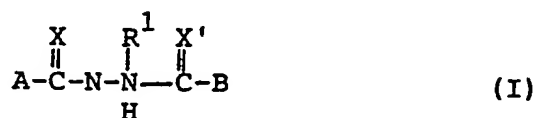
phenalkyl having one to two carbon atoms in the alkyl group and the phenyl ring is unsubstituted or substituted with one or two of the same or different chloro, fluoro, bromo, iodo, methyl, ethyl, methoxy or trifluoromethyl.

6. A composition according to claim 3 wherein
X and X' are O;
 R^1 is t-butyl; and
A is phenyl and B is cyclohexyl, benzyl, 1-cyclohexenyl, 2-methylcyclohexadi-2,5-enyl, phenylethynyl, 1-methylpropyl, 2-methyl-1-phenylbutyl, 3-acetyl-2,2-dimethylcyclobutyl-methyl, 1-butenyl, 3-butenyl, 3-carbomethoxypropyl or methoxymethyl; or
A is 3,5-dichlorophenyl and B is 2-bromoethyl; or
A is 4-chlorophenyl and B is cyclobutyl; or
A is 2,3-dimethylphenyl and B is 1-methylethenyl or 1-ethylethenyl; or
A is 4-ethylphenyl and B is 1-methylethenyl.

7. A composition according to any preceding claim containing the insecticidal compound in an amount of from 0.0001, preferably 0.001, to 99% by weight.
8. A composition according to claim 7 containing the insecticidal compound in an amount of from 0.01 to 99% by weight.
9. A composition according to claims 7 or 8 in the form of a wettable powder, a flowable, a dust, a granule, a bait or an emulsifiable concentrate.
10. A method of controlling insects which comprises contacting said insects with insecticidal compound as defined in any of claims 1 to 6, optionally in a composition according to any of claims 1 to 9.
11. A method according to claim 10 which comprises applying the compound at a rate of from about 10 grams to about 10 kilograms per hectare, to growing plants or to an area where plants are to be grown.
12. A method according to claim 11 wherein the rate of application is 100 grams to 5 kilograms of the compound per hectare.
13. A method according to claim 12 of controlling insects from the order Lepidoptera or Coleoptera.

CLAIMS: ES

1. The use of an insecticidally active compound which is a compound of the formula



wherein

X and X' are the same or different O, S or NR;
 R^1 is unsubstituted branched (C_3 - C_{10})alkyl or straight chain (C_1 - C_4)alkyl substituted with one or two of the same or different (C_3 - C_6)cycloalkyl;

A is unsubstituted or substituted naphthyl where the substituents can be from one to three of the same or different halo; cyano; nitro; hydroxy; (C_1 - C_4)alkoxy; (C_1 - C_4)alkyl; carboxy; (C_1 - C_4)alkoxy-carbonyl; (C_1 - C_4)alkanoyloxy or NH_2 , NHZ or $-\text{NZZ}'$;

unsubstituted or substituted phenyl where the substituents can be from one to five of the same or different halo; nitro; cyano; hydroxy; (C_1 - C_6)alkyl; halo-(C_1 - C_6)alkyl; cyano- (C_1 - C_6)alkyl; (C_1 - C_6)alkoxy; halo-(C_1 - C_6)-alkoxy; (C_1 - C_6)alkoxy- (C_1 - C_6)alkyl having independently the stated number of carbon atoms in each alkyl group; (C_1 - C_6)alkoxy- (C_1 - C_6)alkoxy having independently the stated number of carbon atoms in each alkyl group; $-\text{OCO}_2\text{R}$ group; (C_2 - C_6)alkenyl optionally substituted with halo, cyano, (C_1 - C_4)alkyl, (C_1 - C_4)alkoxy, halo- (C_1 - C_4)alkoxy or (C_1 - C_4)-

alkylthio; carboxy; $-\text{RCO}_2\text{R}'$ group; $-\text{COR}$;
 halo- (C_1-C_6) alkyl-carbonyl; cyano- (C_1-C_6) -
 alkyl-carbonyl; nitro- (C_1-C_6) alkyl-carbonyl;
 (C_1-C_6) alkoxy-carbonyl; halo- (C_1-C_6) -
 alkoxy-carbonyl; $-\text{OCOR}$ group; $-\text{NRR}'$ group;
 amino substituted with hydroxy, (C_1-C_4) alkoxy
 or (C_1-C_4) alkylthio groups; phenylamino;
 diphenylamino; $-\text{CONRR}'$ group; $-\text{OCONRR}'$ group;
 $-\text{NRCOR}'$ group; $-\text{NRCO}_2\text{R}'$ group; $-\text{N}(\text{COR})\text{COR}'$
 group; $-\text{OCONRCOR}'$ group; sulfhydryl; halothio;
 (C_1-C_6) alkylthio; halo- (C_1-C_6) alkylthio; $-\text{SOR}$
 group; $-\text{SO}_2\text{R}$ group; phenylsulfonyl; $-\text{OSO}_2\text{R}$
 group; halo- (C_1-C_6) alkylsulfonyloxy; $-\text{SO}_2\text{NRR}'$
 group; $-\text{NRSOR}'$ group; $-\text{NRSO}_2\text{R}'$ group; $-\text{CSR}$
 group; CS_2R group; $-\text{NRCSR}'$ group; $-\text{SCOR}$ group;
 unsubstituted or substituted phenyl having one
 to three of the same or different halo, cyano,
 nitro, hydroxy (C_1-C_4) alkyl, (C_1-C_4) alkoxy,
 carboxy, (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) -
 alkanoyloxy, NH_2 , NHZ or $-\text{NZZ}'$; phenoxy where
 the phenyl ring is unsubstituted or
 substituted with one to three of the same or
 different halo, cyano, nitro, hydroxy,
 (C_1-C_4) alkyl, (C_1-C_4) alkoxy, carboxy, (C_1-C_4) -
 alkoxy-carbonyl, (C_1-C_4) alkanoyloxy, NH_2 , NHZ
 or $-\text{NZZ}'$; phenylthio where the phenyl ring is
 unsubstituted or substituted with one to three
 of the same or different halo, cyano, nitro,
 hydroxy, (C_1-C_4) alkyl, (C_1-C_4) alkoxy, carboxy,
 (C_1-C_4) alkoxy-carbonyl, (C_1-C_4) alkanoyloxy,
 NH_2 , NHZ or $-\text{NZZ}'$; or when two adjacent
 positions on the phenyl ring are substituted
 with alkoxy groups, these groups may be joined
 to form, together with the carbon atoms to
 which they are both attached, a 5- or 6-

membered dioxolano or dioxano heterocyclic ring;

B is unsubstituted or substituted (C_1-C_{10})alkyl having as the optional substituent(s) one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4)alkoxy, halo-(C_1-C_4)-alkoxy, carboxy, (C_1-C_4)alkoxycarbonyl, (C_1-C_4)alkanoyloxy, phenyl, NH_2 , NHZ or -NZZ'.

unsubstituted or substituted (C_3-C_8)cycloalkyl or unsubstituted or substituted (C_3-C_8)cycloalkyl(C_1-C_4)alkyl, having as the optional substituent(s) one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4)-alkyl, halo-(C_1-C_4)alkyl, (C_1-C_4)alkoxy, halo-(C_1-C_4)alkoxy, carboxy, (C_1-C_4)alkanoyl, (C_1-C_4)alkoxy-carbonyl, (C_1-C_4)alkanoyloxy, NH_2 , NHZ or -NZZ';

unsubstituted or substituted (C_2-C_8)alkenyl or unsubstituted or substituted (C_3-C_8)alkadienyl having, as the optional substituent(s), a furyl, thienyl or pyridyl group or one to four of the same or different halo, cyano, nitro, hydroxy, (C_1-C_4)alkyl, (C_3-C_6)cycloalkyl, halo-(C_1-C_4)alkyl, (C_1-C_4)alkoxy, halo-(C_1-C_4)alkoxy, carboxy, (C_1-C_4)alkoxy-carbonyl, (C_1-C_4)alkanoyloxy, NH_2 , NHZ or -NZZ';

unsubstituted or substituted (C_3-C_8)cycloalkenyl or unsubstituted or substituted (C_3-C_8)cycloalkadienyl having as the optional substituent(s), one to four of the same or different halo, cyano, nitro, hydroxy,

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(C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo-(C₁-C₄)alkoxy, carboxy, (C₁-C₄)-alkoxy-carbonyl, (C₁-C₄)alkanoyloxy, NH₂, NHZ or -NZZ';

unsubstituted or substituted (C₂-C₈)alkynyl having, as optional substituent(s), one to four of the same or different halo, cyano, nitro, hydroxy, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo-(C₁-C₄)alkoxy, carboxy, (C₁-C₄)alkoxy-carbonyl, (C₁-C₄)alkanoyloxy, phenyl, NH₂, NHZ or -NZZ';

phenalkyl having one to four carbon atoms in the alkyl group and wherein the alkyl group is unsubstituted or substituted with one to three of the same or different halo, cyano, hydroxy, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, (C₁-C₄)-alkoxy-carbonyl, NH₂, NHZ or -NZZ', and the phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, cyano-(C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo-(C₁-C₄)alkoxy, carboxy, (C₁-C₄)alkoxy-carbonyl, (C₁-C₄)alkanoyloxy, (C₂-C₆)alkenyl, halo-(C₂-C₆)alkenyl, (C₂-C₆)-alkynyl, NH₂, NHZ or -NZZ'; or

phenalkenyl having two to six carbon atoms in the alkenyl group and the alkenyl group is unsubstituted or substituted with one to three of the same or different halo, cyano, hydroxy, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)-alkoxy, halo-(C₁-C₄)alkoxy, (C₁-C₄)-alkoxy-carbonyl, NH₂, NHZ or -NZZ', and the

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phenyl ring is unsubstituted or substituted with one to three of the same or different halo, cyano, nitro, hydroxy, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy, halo-(C₁-C₄)alkoxy, carboxy, (C₁-C₄)alkoxy-carbonyl, (C₁-C₄)alkanoyloxy or NH₂, NHZ or -NZZ';

where R and R' are hydrogen or (C₁-C₆)alkyl; Z and Z' are (C₁-C₄)alkyl; "amino" means NRR'; or an agronomically acceptable salt thereof; except for such a compound in which X and X' are O, R¹ is t-butyl, A is unsubstituted phenyl and B is unsubstituted methyl or unsubstituted ethyl.

together with agronomically acceptable diluent or carrier to make an insecticidal composition.

2. The use according to claim 1 of the compound wherein

X and X' are O or S; and/or

R¹ is unsubstituted branched (C₃-C₈)alkyl or a straight chain (C₁-C₄)alkyl substituted with one or two of the same or different (C₃-C₄)cycloalkyl; and/or

A is unsubstituted naphthyl; or

unsubstituted or substituted phenyl where the substituents can be from one to three of the same or different halo; nitro, cyano; (C₁-C₄)alkyl; halo-(C₁-C₄)alkyl; cyano-(C₁-C₄)alkyl, (C₁-C₄)alkoxy; (C₁-C₄)alkoxy-(C₁-C₄)alkyl; -COD; carboxy; (C₁-C₄)alkoxy-carbonyl; (C₁-C₄)alkanoyloxy; NH₂, NHZ or -NZZ'; (C₁-C₄)alkylthio; -CSD; -CS₂D; -SCOD; unsubstituted or substituted phenyl having one

active ingredient during this application step so that the rate of application of active insecticidal compound is sufficient to cause an unacceptable or adverse effect on the crop plants or portions of the benzoyl ring are substituted.

with alkoxy groups, these groups are joined to the benzene ring according to claim 10 or 11 which comprises applying the compound or salt at a rate of from about 10 grams to about 10 kilograms per hectare, to growing plants or to an area where plants are to be grown or substituted (C₁-C₈) alkyl

having as the optional substituent(s) one to three of the same or different halo, cyano, (C₁-C₄) alkyl, halo-(C₁-C₄) alkyl, (C₁-C₄) alkoxy, (C₁-C₄) alkanoyl or (C₁-C₄) haloalkoxy;

14. unsubstituted or substituted (C₃-C₆) cycloalkenyl for controlling insects from the order Lepidoptera or Coleoptera, (C₁-C₄) alkyl, having as the optional substituent(s) one or two of the same or different halo, (C₁-C₄) alkyl, halo-(C₁-C₄) alkyl, (C₁-C₄) alkoxy, (C₁-C₄) alkanoyl or (C₁-C₄) haloalkoxy;

unsubstituted or substituted (C₂-C₆) alkenyl having as the optional substituent(s) a furyl or one to three of the same or different (C₁-C₄) alkyl, halo-(C₁-C₄) alkyl, (C₁-C₄) alkoxy or halo-(C₁-C₄) alkoxy;

unsubstituted or substituted (C₃-C₆) cycloalkenyl having as the optional substituent(s) one or two of the same or different halo, (C₁-C₄) alkyl, halo-(C₁-C₄) alkyl, (C₁-C₄) alkoxy or halo-(C₁-C₄) alkoxy;

unsubstituted or phenyl substituted alkynyl;

phenalkyl having one or two carbon atoms in the alkyl group and the alkyl group is unsubstituted or substituted with one or two of the same or different halo, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy or halo-(C₁-C₄)alkoxy and the phenyl ring is unsubstituted or substituted with one or two of the same or different halo, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy or halo-(C₁-C₄)alkoxy; or

phenalkenyl having two or three carbon atoms in the alkenyl group and the alkenyl group is unsubstituted or substituted with halo, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)-alkoxy or halo-(C₁-C₄)alkoxy and the phenyl ring is unsubstituted or substituted with one or two of the same or different halo, (C₁-C₄)-alkyl, halo-(C₁-C₄)alkyl, (C₁-C₄)alkoxy or halo-(C₁-C₄)alkoxy; or an

agronomically acceptable salt thereof; wherein D is hydrogen or (C₁-C₄)alkyl and Z and Z' are (C₁-C₄)alkyl.

3. The use according to claim 2 of a compound wherein

X and X' are O or S; and/or

R¹ is branched (C₃-C₈)alkyl; and/or

A is unsubstituted naphthyl; or

unsubstituted or substituted phenyl having one to three of the same or different halo, nitro, cyano, (C₁-C₄)alkyl, halo-(C₁-C₄)alkyl, cyano-(C₁-C₄)alkyl, (C₁-C₄)alkoxy, -COD, (C₁-C₄)-

alkoxy-carbonyl, (C₁-C₄)alkanoyloxy, or
unsubstituted or substituted phenyl having one
or two of the same or different halo, nitro,
(C₁-C₄)alkyl, (C₁-C₄)alkoxy, carboxy, (C₁-C₄)-
alkoxy-carbonyl, (C₁-C₄)alkanoyloxy, NH₂, NHZ
or -NZZ'; and/or

B is unsubstituted or substituted (C₁-C₆)alkyl
having one to three of the same or different
halo, cyano, (C₁-C₄)alkoxy, phenyl, (C₁-C₃)-
alkoxy-carbonyl or halo-(C₁-C₄)alkoxy;

unsubstituted or substituted (C₃-C₆)cycloalkyl
or unsubstituted or substituted (C₃-C₆)-
cycloalkyl-(C₁-C₄)alkyl where the optional
substituent is halo, (C₁-C₄)alkyl, (C₁-C₄)-
alkanoyl, (C₁-C₄)alkoxy or halo-(C₁-C₄)alkoxy;

unsubstituted or substituted (C₂-C₆)alkenyl
having one or two of the same or different
(C₁-C₄)alkyl, (C₁-C₄)alkoxy or halo-(C₁-C₄)-
alkoxy;

unsubstituted or substituted (C₄-C₆)cyclo-
alkenyl where the substituent is halo,
(C₁-C₄)alkyl, (C₁-C₄)alkoxy or halo-(C₁-C₄)-
alkoxy; or

unsubstituted or phenyl-substituted alkynyl;
or an

agronomically acceptable salt thereof.

4. A compound according to claim 3 of the compound
wherein

X and X' are O; and/or

R¹ is branched (C₄-C₇)alkyl; and/or
A is unsubstituted, monosubstituted, 2,3-disubstituted or 2,4-disubstituted phenyl where the substituents can be the same or different halo, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, or halo-(C₁-C₄)alkyl; and/or
B is unsubstituted or substituted (C₁-C₆)alkyl having one to three of the same or different halo, phenyl or cyano;

unsubstituted (C₄-C₆)cycloalkyl;

unsubstituted or substituted (C₂-C₅)alkenyl having as the optional substituent(s) one or two of the same or different (C₁-C₄)alkyl;

unsubstituted (C₄-C₆)cycloalkenyl; or

phenalkyl having one or two carbon atoms in alkyl group and the phenyl ring is unsubstituted or substituted with one or two of the same or different halo, (C₁-C₄)alkyl, or (C₁-C₄)alkoxy;

or an agronomically acceptable salt thereof.

5. The use according to claim 4 of the compound wherein

X and X' are O; and/or

R¹ is t-butyl, neopentyl (2,2-dimethylpropyl) or 1,2,2-trimethylpropyl; and/or

A is unsubstituted or monosubstituted phenyl where the substituent can be chloro, fluoro, bromo, iodo, methyl, ethyl, methoxy or trifluoromethyl; and/or

B is unsubstituted or substituted (C_1-C_4)alkyl having as the optional substituent(s) one to three of the same or different, phenyl, chloro, fluoro or bromo;

unsubstituted (C_4-C_6)cycloalkyl;

unsubstituted (C_4-C_6)cycloalkenyl; or

phenalkyl having one to two carbon atoms in the alkyl group and the phenyl ring is unsubstituted or substituted with one or two of the same or different chloro, fluoro, bromo, iodo, methyl, ethyl, methoxy or trifluoromethyl; or an agronomically acceptable salt thereof.

6. The use according to claim 3 of the compound wherein

X and X' are O;

R^1 is t-butyl; and

A is phenyl and B is cyclohexyl, benzyl, 1-cyclohexenyl, 2-methylcyclohexadi-2,5-enyl, phenylethynyl, 1-methylpropyl, 2-methyl-1-phenylbutyl, 3-acetyl-2,2-dimethylcyclobutyl-methyl, 1-butenyl, 3-butenyl, 3-carbomethoxypropyl or methoxymethyl; or

A is 3,5-dichlorophenyl and B is 2-bromoethyl; or

A is 4-chlorophenyl and B is cyclobutyl; or

A is 2,3-dimethylphenyl and B is 1-methylethenyl or 1-ethylethenyl; or

A is 4-ethylphenyl and B is 1-methylethenyl.

7. The use according to any preceding claim of the compound or salt in an amount of from 0.0001, preferably 0.001, to 99% by weight of the composition.
8. The use according to claim 6 of the compound or salt in an amount of from 0.01 to 99% by weight of the composition.
9. The use according to any of claims 6 to 8 of the compound or salt to make a composition in the form of a wettable powder, a flowable, a dust, a granule, a bait or an emulsifiable concentrate.
10. The use of a compound or salt as defined in any of claims 1 to 6, optionally in a composition also containing agronomically acceptable diluent or carrier, for controlling insects, by contacting said insects with an insecticidally effective amount of said compound or salt.
11. A mechanical process for improving the commercial value and/or profitability of vendible crops from plants whose growth is affected or likely to be affected by insects comprising (1) charging to a container, fumigation device or mechanical dissemination device an insecticidal compound or salt as defined in any of claims 1 to 6, optionally in a mixture with agronomically acceptable diluent or carrier, (2) using the container, fumigator or mechanical dissemination device to apply the insecticidal compound or salt, in the form of granules, dust, smoke, vapour or surfactant-containing liquid preparation to growing plants or to a growth medium where the plants are growing or are to be grown, or to the insects themselves, (3) controlling the dose of the



DOCUMENTS CONSIDERED TO BE RELEVANT			EP 87301730.5
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A	AT - B - 205 488 (MERCK & CO) * Claim 1 * --	1	C 07 C 109/10 C 07 D 307/54 A 01 N 37/28
A	GB - A - 1 573 668 (KUREHA KAGAKU KOGYO) * Claim 1 * --	1	
A	FR - A - 2 120 185 (CHINOIN GYOGYSZER) * Claim 1 * --	1	
A	US - A - 3 773 830 (MARTIN DEXTER) * Abstract * ----	1	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 07 C 109/00
Place of search VIENNA		Date of completion of the search 04-05-1987	Examiner REIF
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document</p>			